

# Argonne National Laboratory

## LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

### Part IX. The Fluid-bed Fluorination of Plutonium-containing Simulated Oxidic Nuclear Fuel in a 1½-inch-diameter Reactor

by

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M. J. Steindler, J. J. Stockbar,  
T. D. Baker, W. H. Gunther,  
and G. W. Redding

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### ABSTRACT

Fluid-bed fluorination of simulated oxidic nuclear fuels containing plutonium was investigated. This work was performed to determine the best reaction conditions for the conversion of the uranium and plutonium content of the simulated nuclear fuel to their respective hexafluorides. The experimental work involved the fluid-bed fluorination of mixtures containing  $U_3O_8$ ,  $PuO_2$ , nonradioactive fission-product (F.P.) element oxides, and alumina. The uranium-to-plutonium weight ratio in the mixtures was 1000:4, and the uranium-to-alumina weight ratio was 1:2. The F.P. mixture contained the following oxides:  $La_2O_3$ ,  $CeO_2$ ,  $Pr_6O_{11}$ ,  $Nd_2O_3$ ,  $Sm_2O_3$ ,  $Eu_2O_3$ ,  $Gd_2O_3$ ,  $Y_2O_3$ ,  $BaO$ ,  $ZrO_2$ , and  $MoO_3$ .

The experimental results showed that more than 99% of the uranium could be removed from the alumina bed at reaction temperatures of 450-500°C. However, a temperature of 550°C and a reaction time of 10 hr were needed to satisfactorily remove plutonium from the alumina bed. A 20-hr fluorination, employing periods of 5 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C, resulted in the removal of 96-98% of the plutonium from the alumina. The recovery of plutonium can be further increased to >99% by reuse of the alumina bed for several additions and fluorinations of the  $U_3O_8$ - $PuO_2$ -F.P. mixture.

The plutonium retention on the alumina was not affected by the type of  $U_3O_8$ - $PuO_2$  powdered mixture, whether derived from a solid solution of  $UO_2$  and  $PuO_2$  or from an intimate mixture of  $U_3O_8$  and  $PuO_2$ . Other factors, which also had no effect on the retention of plutonium, included variation in the type of alumina used as bed material (sintered or fused granules), the particle-size range of the alumina, and the presence of stainless-steel de-cladding products. However, the plutonium retention on the alumina was affected by the flowrate of the fluorinating gas and by the quantity of fission products or plutonium in the solid reaction mixture.

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Autoradiographs of sectioned alumina granules from an alumina bed used for the fluorination of a  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$ -F.P. mixture showed that the retained plutonium was exclusively in the surface and not distributed in the body of the particles.

## I. INTRODUCTION

Fluid-bed fluoride volatility processes are being developed for the processing of spent nuclear-power-reactor fuel. One of these processes is designed to recover uranium and plutonium values from low-enrichment, stainless-steel or Zircaloy-clad, uranium dioxide fuels. The ANL reference flowsheet<sup>1</sup> for reprocessing Zircaloy-clad,  $\text{UO}_2$  fuel involves the following steps: (1) removal of the Zircaloy cladding by reacting it with gaseous  $\text{HCl}$  to form volatile  $\text{ZrCl}_4$ , with subsequent conversion of  $\text{ZrCl}_4$  to the solid oxide in a second vessel by reaction with steam (pyrohydrolysis); (2) fluorination of the uranium and plutonium oxides to the hexafluorides,  $\text{UF}_6$  and  $\text{PuF}_6$ ; (3) separation of the  $\text{PuF}_6$  from  $\text{UF}_6$  by thermal decomposition of  $\text{PuF}_6$  to solid  $\text{PuF}_4$ ; and (4) decontamination of the  $\text{UF}_6$  by fractional distillation, aided by adsorption techniques. This report presents the results of one of a series of laboratory investigations in support of this program; specifically, this report concerns fluid-bed fluorination of simulated oxide fuel containing plutonium.

A previous report<sup>2</sup> described boat-reactor experiments on the fluorination of mixtures containing uranium and plutonium oxides, nonradioactive F.P. element oxides, and alumina. That work defined the reaction conditions of temperature and time necessary for efficient removal of uranium and plutonium from these mixtures, and the effect of the presence of fission products on the plutonium retention on the alumina. A subsequent report<sup>3</sup> described the development of a  $1\frac{1}{2}$ -in.-diam, fluid-bed reactor system for a study of the fluorination of  $\text{U}_3\text{O}_8$ . The apparatus and procedures developed during that work<sup>3</sup> were employed in the fluid-bed study described in this report.

The uranium dioxide fuel elements, after the decladding step, would be present in the fluid bed as pellets, pellet fragments, and powder. Fluorination of material of such a random-size distribution would result in erratic fluorination rates and undesirably erratic rates of production of  $\text{UF}_6$ . A scheme involving the oxidation of the fuel elements at 400 to 500°C has been proposed to convert the randomly sized fuel elements to a uniform powder. This oxidative treatment results in a finely divided mixture of  $\text{U}_3\text{O}_8$  and  $\text{PuO}_2$ . The oxidation of the pellets can be carried out in the lower portion of a fluid bed and the transported powder fluorinated in the upper portion of the fluid bed. This two-zone, oxidation-fluorination procedure was demonstrated in a semipilot-plant scale<sup>4</sup> by using unirradiated  $\text{UO}_2$  pellets. In previously reported, laboratory-scale,  $1\frac{1}{2}$ -in.-diam, fluid-bed work,<sup>3</sup>

the fluorination portion of the two-zone procedure was simulated by feeding finely divided  $U_3O_8$  powder into the fluid bed at controlled rates and contacting the powder with fluorine at a point just above the entry point of the powder. The laboratory work showed that fluorination could be satisfactorily performed at feed rates of  $U_3O_8$  of 5 g/min, corresponding to  $UF_6$  production rates of 50 lb/hr-ft<sup>2</sup> of reactor cross section. The techniques developed in this laboratory-scale work were employed in the work described in this report. In addition, previously reported boat-reactor experiments<sup>2</sup> had shown that plutonium was more readily fluorinated from mixtures of  $U_3O_8$  and  $PuO_2$  produced by the oxidation of  $UO_2$ - $PuO_2$  solid solutions than from powdered  $UO_2$ - $PuO_2$  solid solution. The reaction conditions found in the boat-reactor study, which resulted in retention of less than 0.01 w/o plutonium on the fluid-bed alumina, employed two 10-hr reaction periods: the first at 450°C using 10% fluorine in nitrogen, and the second at 550°C using 75% fluorine in nitrogen.

The charge from a power reactor, such as the Dresden Reactor, will probably consist of 100 kg of uranium, 0.4 kg of plutonium, and about 1 kg of fission products. This charge will be mixed with about 200 kg of refractory-grade alumina as the fluidized medium. A previous report<sup>2</sup> considered the economic factors attending a loss of 1% of the plutonium charged to the reactor. The present experiments used a 1% loss of plutonium by retention on the alumina as a maximum acceptable loss level. In the present work, the retention of 1% of the plutonium charged to the reactor on the alumina corresponds to a concentration of 0.002 w/o plutonium on the alumina. In the previous boat-reactor experiments,<sup>2</sup> about a sixth as much alumina was used and a 1% loss of plutonium corresponded to a plutonium concentration on the alumina of 0.007 w/o. Both of these loss estimates are based on the practice of discarding the fluid-bed alumina after each fluorination.

The present report presents the results of extensive experimental work on the fluid-bed fluorination of uranium-plutonium oxide mixtures in a 1½-in.-diam reactor. The experimental work involved exploration of the effect of the variation in reaction conditions and materials on the conversion of uranium and plutonium to their respective volatile hexafluorides. During this work, the effect of several variables on plutonium retention on the alumina was determined: (1) the source of plutonium, whether present in a  $UO_2$ - $PuO_2$  solid solution or as  $PuO_2$ ; (2) the addition of bismuth to the alumina; (3) the quantity of plutonium and fission products fed to the reactor in a single experiment; (4) the use of a static rather than a fluidized bed; (5) variation in the fluorinating gas flowrate; and, (6) the type of alumina used as the fluid bed. Experiments were also performed to evaluate the reuse of an alumina bed for the fluorination of several batches of uranium-plutonium oxide mixture, and to determine the effect on the fluorination reaction of the presence of stainless-steel decladding product in the feed material. An autoradiographic technique was used to determine the location of plutonium retained on the alumina particles. And finally, the efficiency of nitric acid leaching for removing plutonium retained on the fluid-bed alumina was studied briefly.

## II. EXPERIMENTAL PROCEDURE

### A. Materials

The  $\text{U}_3\text{O}_8$  used in this work to prepare  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixtures was obtained from Union Carbide Nuclear Company. The material had a surface area of 0.74 sq m/g, as measured by nitrogen adsorption, and consisted of particles with an average diameter of 3.1 microns. Chemical analysis of the  $\text{U}_3\text{O}_8$  indicated a uranium content of 84.46% (theoretical: 84.80%). Plutonium for these mixtures was obtained from two general sources: from  $\text{UO}_2$ - $\text{PuO}_2$  solid solution in the form of pellets nominally containing 83% uranium and 4% plutonium, and from various batches of powdered  $\text{PuO}_2$ .

Commercial-grade fluorine, which was passed through a sodium fluoride trap at 100°C to remove HF, was used. The nitrogen, which was used as the fluidizing gas and also as a diluent for the fluorine, was passed through a trap containing molecular sieves to remove water.

A mixture of nonradioactive F.P. element oxides was used to represent F.P. concentrations in the  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixtures. A group of these ( $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ , and  $\text{Y}_2\text{O}_3$ ) was obtained from the Lindsay Chemical Division of American Potash and Chemical Company and was of a purity of 99.9% or greater. Other compounds ( $\text{BaO}$ ,  $\text{ZrO}_2$ , and  $\text{MoO}_3$ ) were reagent-grade chemicals and had stated purities of 99% or greater.

Two types of alumina were used in this work as the inert fluid-bed material. One of these, Type RR\* (high-purity) fused alumina, was available both as a nominal 120-mesh material with a median particle size of 90 microns and a particle-size range of 50-150 microns and as a nominal 60-mesh material with a median particle size of 200 microns and a particle-size range of 150-250 microns. The other alumina was Type T-61\*\* having a median particle size of 150 microns and a particle-size range of 80-250 microns. Sieve analyses for the three batches of alumina used as the fluid-bed material are listed in Table I.

The mixtures of  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  or  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$ -F.P. element oxides were prepared in the following manner: Sufficient quantities of  $\text{U}_3\text{O}_8$ , oxidized  $\text{UO}_2$ - $\text{PuO}_2$  pellets ( $\text{U}_3\text{O}_8$ - $\text{PuO}_2$ ) or  $\text{PuO}_2$ , and a mixture of F.P. oxides were intimately mixed to produce a mixture having a uranium-to-plutonium ratio of 1000:4 and a uranium-to-fission-product mixture ratio of 100:1. The F.P. element oxides used and their proportions in the  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixture are listed in Table II. After the mixtures were blended for about 10 hr, random samples were taken for uranium and plutonium analyses. The analytical results for a typical batch showed  $0.386 \pm 0.001$  w/o plutonium and  $80.5 \pm 0.2$  w/o uranium. The F.P. oxide concentration in the mixture, based on the weight of oxides added, was 0.86 w/o.

\*Product of the Norton Co.

\*\*Product of the Aluminum Company of America.



TABLE I. Sieve Analysis of Alumina Used in Fluid-bed Experiments

U. S. Sieve Designation	Percentage of Alumina
1. 120 Mesh, Type RR	
+120	6.0
-120 +140	21.0
-140 +170	26.0
-170 +200	32.0
-200 +230	10.0
-230 +270	3.0
-270	2.0
2. 60 Mesh, Type RR	
+40	0.3
-40 +60	77.2
-60 +80	21.6
-80 +100	0.6
-100 +170	0.3
3. 100 Mesh, Tabular T-61	
+45	0.1
-45 +60	5.3
-60 +80	47.6
-80 +120	38.7
-120 +170	6.3
-170 +230	1.1
-230	0.9

TABLE II. Composition of  $U_3O_8$ - $PuO_2$  F.P. Oxide Mixture<sup>a</sup>

Material	Part of Mixture, w/o
$Gd_2O_3$	0.0004
$Eu_2O_3$	0.002
$Y_2O_3$	0.026
$Sm_2O_3$	0.040
$Pr_6O_{11}$	0.042
$La_2O_3$	0.050
BaO	0.058
$CeO_2$	0.090
$Nd_2O_3$	0.173
$ZrO_2$	0.182
$MoO_3$	0.187
$PuO_2$	0.4
$U_3O_8$	Balance

<sup>a</sup>Representative of spent Dresden-type fuel after 10,000 MWd/ton burnup, 4 yr in reactor, 30-day cooled.

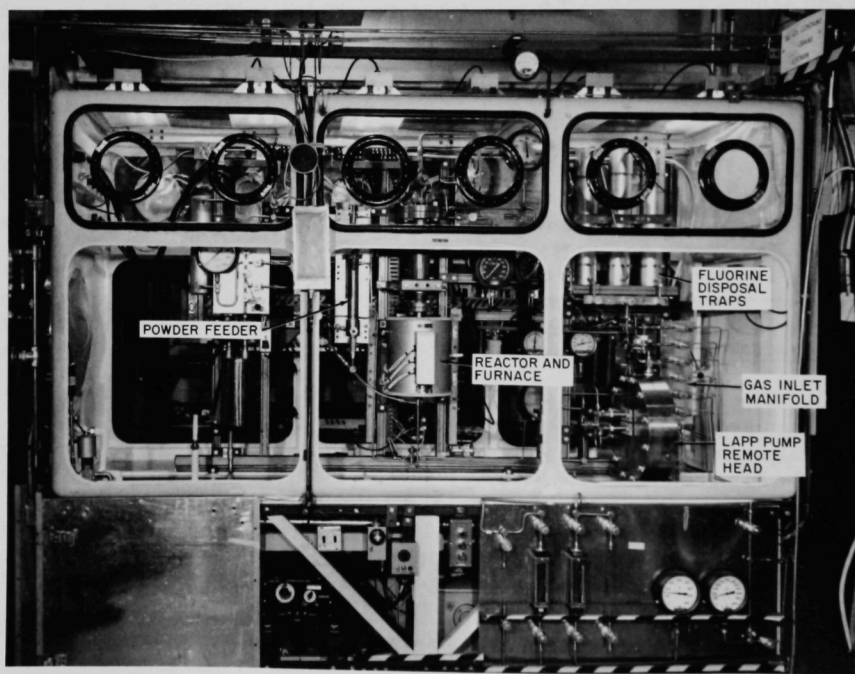
## B. Apparatus

The fluid-bed apparatus used in this work was similar to the apparatus used for the fluorination of  $U_3O_8$  and described previously.<sup>3</sup> The apparatus consisted of the following major components: (1) a  $1\frac{1}{2}$ -in.-diam fluid-bed fluorinator; (2) a powder feeder; (3) a system of cold traps, used to condense the  $UF_6$ - $PuF_6$  product; (4) a Lapp diaphragm pump employing a remote head, used to circulate the gas phase; (5) activated alumina traps for the disposal of fluorine; and (6) manifolds supplying fluorine, nitrogen, and vacuum service. All the apparatus was contained within an alpha glove-box and was manipulated through gloveports. The alpha glovebox, the detailed description of which has been published,<sup>5</sup> was three modules in length

and  $1\frac{1}{2}$  modules in height. (A module is a cube 40 in. on edge.) Figure 1 is a photograph of one face of the alpha box showing the placement of the apparatus before all the windows and gloves had been put in place. Figure 2 shows a close-up view of the fluid-bed reactor.

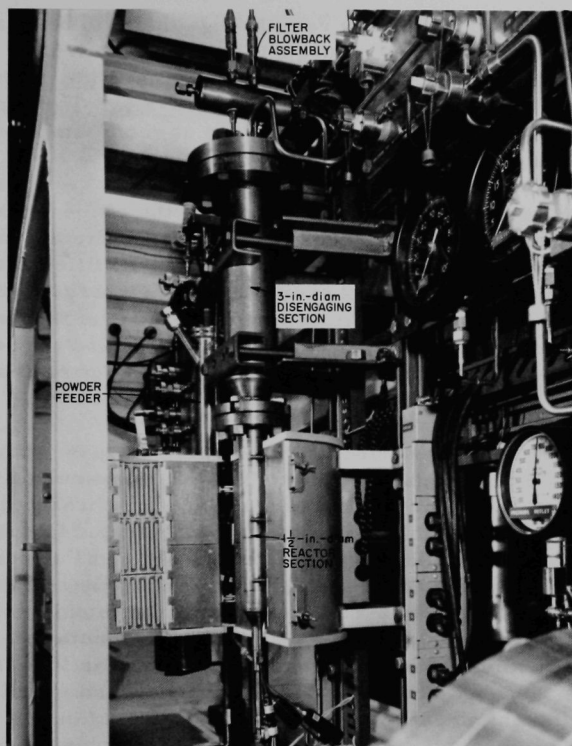
### 3. Procedure

Two reaction periods were used for the fluorinations of the  $U_3O_8$ - $PuO_2$  mixtures. In the first period (the feeding-fluorination period) the  $U_3O_8$ - $PuO_2$  powder was injected into the fluid bed and immediately contacted with a fluorine-containing gas stream. During this period, about 99% of the uranium was converted to  $UF_6$ , and between 40 and 70 w/o of the plutonium was converted to  $PuF_6$ . The feeding-fluorinations were performed at 450 and 500°C for reaction times of 1 to 5 hr, depending on the rate of feed of the  $U_3O_8$ - $PuO_2$  mixture. In the second period (the recycle-fluorination period), the fluorine content was raised to about 100% and the gas was cycled through the Lapp pump and returned to the fluidized bed. The reaction temperature during the recycle-fluorination period was varied over the range of 450-550°C. This recycle-fluorination period was intended to remove essentially all the remaining uranium and plutonium from the alumina bed material.



108-6080

Fig. 1. The  $1\frac{1}{2}$ -in.-diam Fluid-bed Reactor System in the Alpha Glovebox



108-6077

Fig. 2. The  $1\frac{1}{2}$ -in.-diam Fluid-bed Reactor

The general operating procedure for the fluorinations was as follows: About 400 g of 120-mesh fused alumina was placed in the fluid-bed fluorinator, which was then heated to the operating temperature, 450 or 500°C. During the heating period, the nitrogen flow, sufficient to fluidize the bed, was started. A charge of a mixture of 300 g of  $U_3O_8$ - $PuO_2$  and 150 g of alumina was placed in the powder feeder. (Alumina was mixed with the  $U_3O_8$ - $PuO_2$  to improve the flow characteristics of the oxide powder.) When the reactor reached the proper operating temperature, the fluorine was fed into the bed through a gas distributor cone (see Reference 3, Fig. 2). The fluorine, which was 20 v/o of the total flow, was diluted with an equal quantity of nitrogen before it entered the bed. The  $U_3O_8$ - $PuO_2$ -alumina mixture was introduced into the fluidizing nitrogen stream, and then into the fluid bed at a point below the fluorine inlet, at a rate of from 1 to 5 g of  $U_3O_8$ - $PuO_2$  mixture per minute. The gas velocity in the  $3/8$ -in.-diam fluidizing-nitrogen inlet line into which the  $U_3O_8$ - $PuO_2$

was fed was 5 ft/sec. Total flow rate through the fluid bed was 12 liters/min (measured at room temperature and 1.32 atm pressure); the fluidizing nitrogen contributed approximately 7 liters/min, and the mixture of fluorine and nitrogen contributed approximately 5 liters/min. The superficial gas velocity in the fluid bed was about 0.4 ft/sec at room temperature (about 1.0 ft/sec at 500°C).

During the feeding-fluorination period, the effluent gas stream from the fluorinator passed through three cold traps, a sodium fluoride trap to remove the  $\text{UF}_6$  and  $\text{PuF}_6$ , and finally through a trap filled with activated alumina to remove the excess fluorine before discharge to the glovebox atmosphere. After the feeding-fluorination period, the fluorine content of the gas phase was increased to approximately 100% and the recycle period was started. During the recycle period, the gas was passed only through the cold traps.

After the reaction period had been completed, the sodium fluoride trap and the cold traps (maintained at  $-78^\circ\text{C}$ ) were evacuated to remove the noncondensable gas from the cold traps and the unreacted gas from the sodium fluoride trap. The cold traps were warmed to room temperature and then weighed to obtain the amount of  $\text{UF}_6$  and  $\text{PuF}_6$  collected. The alumina, which was used as the fluid-bed medium, was removed from the reactor, and samples were taken for uranium and plutonium analyses.\* The small quantity (about 1-2 g) of a mixture of uranium and plutonium fluorides and alumina, which was generally retained in the disengaging section of the fluid-bed reactor, was also removed and submitted for uranium and plutonium analyses.

Prior to the tests with mixtures of  $\text{U}_3\text{O}_8$  and  $\text{PuO}_2$ , experiments using  $\text{U}_3\text{O}_8$  alone were conducted to determine the efficiency of the cold traps for collection of  $\text{UF}_6$ . Nine experiments were performed in which the feeding-fluorination period at  $500^\circ\text{C}$ , using 20 v/o fluorine, was followed by a recycle-fluorination period of 5 hr at  $500^\circ\text{C}$ , using 100% fluorine. The average results for these experiments showed a conversion of  $99.7 \pm 0.1\%$  of the  $\text{U}_3\text{O}_8$  to  $\text{UF}_6$  and a cold-trapping efficiency of 99.3%.

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\*The technique developed for obtaining representative samples of the fluid bed, and the analytical procedures used for determining uranium and plutonium, are given in Appendix A.



### III. RESULTS AND DISCUSSION

#### A. Effect of Temperature, Reaction Time, and Presence of Nonradioactive Fission Products on the Conversion of Plutonium and Uranium to Hexafluorides

The first experiments involving plutonium used  $U_3O_8$ - $PuO_2$  mixtures that did not contain F.P. oxides. In all the experiments, the feeding-fluorination period was performed at  $500^\circ C$ , using 20 v/o fluorine in nitrogen. A mixture of 300 g of  $U_3O_8$ - $PuO_2$  and 150 g of  $Al_2O_3$  was fed into a 400-g bed of  $Al_2O_3$  at a rate of about 5 g of  $U_3O_8$ - $PuO_2$  per minute. Each feeding-fluorination period was followed by a recycle-fluorination period at either  $500$  or  $550^\circ C$  for 5 or 15 hr using 100% fluorine. In one experiment, which was terminated after the feeding-fluorination period, the alumina bed contained 0.043 w/o uranium and 0.063 w/o plutonium. If no reaction to form  $UF_6$  and  $PuF_6$  had occurred, the uranium and plutonium concentrations in the alumina bed would have been 31.5 w/o uranium and 0.14 w/o plutonium. The results for experiments in which the feeding-fluorination period was followed by a recycle-fluorination period are listed in Section A of Table III. After a recycle fluorination at  $500^\circ C$  for 5 hr, the uranium and plutonium concentrations on the alumina were 0.021 and 0.033 w/o, respectively; after a recycle fluorination at  $550^\circ C$  for 5 hr, the uranium and plutonium concentrations on the alumina were 0.003 and 0.022 w/o, respectively. Extending the recycle-fluorination period to 15 hr resulted in concentrations on the alumina of 0.007 w/o uranium and 0.030 w/o plutonium at  $500^\circ C$ , and 0.014 w/o uranium and 0.011 w/o plutonium at  $550^\circ C$ . In these fluid-bed experiments, the alumina-to-uranium ratio was about 2:1; in the boat experiments previously reported,<sup>2</sup> the alumina-to-uranium ratio was 1:3. A residual plutonium concentration of 0.01 w/o on the alumina in these fluid-bed experiments represents about 5% of the plutonium fed to the reactor for a single use of alumina; for the boat experiments previously reported,<sup>2</sup> a plutonium concentration of 0.01 w/o on the alumina represented about 1% of the plutonium involved in the experiment.

A second set of experiments was performed using  $U_3O_8$ - $PuO_2$  mixtures containing F.P. oxides. In one experiment, which was terminated after the feeding-fluorination period, the alumina bed contained 0.149 w/o uranium and 0.106 w/o plutonium. If no reaction to form  $UF_6$  and  $PuF_6$  had occurred, the uranium and plutonium concentrations in the alumina bed would have been 30.4 w/o uranium and 0.15 w/o plutonium. The results for experiments in which the feeding-fluorination period was followed by a recycle-fluorination period are listed in Section B of Table III. These results show concentrations on the alumina of 0.016 w/o uranium and 0.057 w/o plutonium after 5 hr of fluorination at  $500^\circ C$ , and 0.017 w/o uranium and 0.038 w/o plutonium after 5 hr of fluorination at  $550^\circ C$ . After 15 hr of recycle fluorination at  $550^\circ C$ , the uranium and plutonium concentrations on the alumina bed were 0.021 and 0.029 w/o, respectively.

TABLE III. Fluid-bed Fluorination of  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  Mixtures:  
Effect of Reaction Temperature and Time

Feeding-fluorination Period

Bed temperature:	500°C
Total gas flow rate:	12 liters/min (at room temp and 1.32 atm)
Gas velocity:	0.98 ft/sec
Fluorine concentration:	20 v/o
Alumina in bed:	400 g
Alumina in feed:	150 g
$\text{U}_3\text{O}_8$ - $\text{PuO}_2$ feed:	300 g
$\text{U}_3\text{O}_8$ - $\text{PuO}_2$ feed rate:	~5 g/min

Recycle-fluorination Period

Total gas flow rate:	8 liters/min (at 1.32 atm)
Linear velocity of gas phase:	0.67 ft/min (at 500°C)
Fluorine concentration:	100%
Conditions:	As indicated

Recycle Periods		Concentration in Al <sub>2</sub> O <sub>3</sub> Bed			
Temp, °C	Time, hr	U		Pu	
		w/o	g	w/o	g
A. <u>No fission products present<sup>a</sup></u>					
500	5	0.021	0.120	0.033	0.187
550	5	0.003	0.016	0.022	0.124
500	15	0.007	0.041	0.030	0.157
550	15	0.014	0.075	0.011	0.056
B. <u>Fission products present<sup>b</sup></u>					
500	5	0.016	0.069	0.057	0.330
550	5	0.017	0.096	0.038	0.220
550	15	0.021	0.117	0.029	0.165
450-500-550 <sup>c</sup>	20	0.015	0.085	0.007	0.040

<sup>a</sup> $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixture contained 253 g of uranium and 1.05 g of plutonium.

<sup>b</sup> $\text{U}_3\text{O}_8$ - $\text{PuO}_2$ -F.P. oxides mixture contained 241 g of uranium, 1.13 g of plutonium and 2.58 g of a mixture of F.P. oxides containing the following oxides:  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{ZrO}_2$ , and  $\text{MoO}_3$  (see Table II).

<sup>c</sup>Feeding-fluorination period: 3 hr at 450°C,  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  feed rate ~2 g/min. Recycle-fluorination periods: 5 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C.

In these experiments, the presence of F.P. oxides in the  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixtures did not materially increase the uranium retention on the alumina; in all cases, the quantities of uranium retained represented less than 1% of that fed to the reactor. However, the presence of fission products in the  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixture did result in a significant increase in the plutonium retention on the alumina.\* These results are similar to those previously obtained for the boat-reactor experiments.<sup>2</sup> In the boat experiments, the plutonium concentration in the alumina for non-F.P. and F.P. experiments at 450°C were 0.027 and 0.065 w/o, respectively.

In one experiment (last entry of Section B of Table III), a lower temperature of 450°C was used both during the feeding-fluorination period and during the initial 5 hr of the recycle-fluorination period. The  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  feed rate was about 2 g/min. These two periods at 450°C were followed by recycle-fluorinations of 5 hr at 500°C and 10 hr at 550°C. After this experiment, the alumina bed contained 0.015 w/o uranium and 0.007 w/o plutonium. The choice of reaction conditions for this experiment was based on results obtained during the boat-reactor experiments,<sup>2</sup> in which these reaction conditions also resulted in plutonium concentrations on the alumina of 0.007 w/o.

## B. Factors Affecting the Retention of Plutonium on Alumina

### 1. Evaluation of the Source of Plutonium

A series of experiments was performed to evaluate the effect of the source of plutonium on the extent of removal of plutonium from a fluid bed by fluorination. Data were obtained for  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  feed material, derived from a  $\text{UO}_2$ - $\text{PuO}_2$  solid solution which was oxidized to produce a mixture of  $\text{U}_3\text{O}_8$  and  $\text{PuO}_2$ , and a feed material in which the  $\text{U}_3\text{O}_8$  and  $\text{PuO}_2$  were present as a physical mixture. The use of a physical mixture rather than a solid solution would afford savings in material costs for experiments on a pilot-plant scale.

The reaction conditions used in these experiments were those that previously resulted in retention of less than 0.01 w/o plutonium on the alumina (see Table III, Section B, entry 4). The feeding-fluorination period was performed at 450°C with a feed rate of about 2 g/min of  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$ , followed by recycle-fluorination periods of 5 hr each at 450 and 500°C and 10 hr at 550°C.

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\*The effect of fission products on the plutonium retention on alumina cited in this section appears valid only in cases in which appreciable plutonium remains on the alumina, as the 0.03 to 0.06 w/o retained for the experiments listed in Table III. For experiments in which less than 0.01 w/o plutonium was retained on the alumina (cf. Section A of Table V), no effect of the presence of the nominal quantity of fission products upon plutonium retention on alumina was noted.

The experimental conditions and results of these experiments are listed in Table IV. A comparison of the first four entries in Table IV indicates that the source of the  $\text{PuO}_2$  does not affect the plutonium retention on the alumina. In one experiment, the feed rate during the feeding-fluorination period was 5 g/min, rather than the 2 g/min or less used in the first experiments. The former experiment resulted in a plutonium retention

TABLE IV. Fluid-bed Fluorination of  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$ -F.P. Mixtures: Effect of Low Temperature during Feeding-fluorination Period and Source of  $\text{PuO}_2$  on Plutonium Retention on Alumina

<u>Feeding-fluorination Period</u>								
Temperature:					450°C			
Total gas flow rate:					12 liters/min (at room temp and 1.32 atm)			
Gas velocity:					0.80 ft/sec			
Fluorine concentration:					20 v/o			
Alumina in bed:					400 g			
Alumina in feed:					170 g, 1U:2Al <sub>2</sub> O <sub>3</sub>			
U <sub>3</sub> O <sub>8</sub> -PuO <sub>2</sub> -fission products:					300 g			
<u>Recycle-fluorination Period</u>								
Recycle periods:					(1) 450°C, 5 hr; (2) 500°C, 5 hr; (3) 550°C, 10 hr			
Total gas flow rate:					8 liters/min (at 1.32 atm)			
Linear velocity of gas phase:					0.67 ft/sec (at 500°C)			
Fluorine concentration:					100%			
Source of PuO <sub>2</sub>	U <sub>3</sub> O <sub>8</sub> -PuO <sub>2</sub> Feed Rate, g/min	<u>Feed Mixtures, g</u>			<u>Concentration in Al<sub>2</sub>O<sub>3</sub> Bed</u>			
					<u>U</u>		<u>Pu</u>	
		U	Pu	F.P.	w/o	g	w/o	g
A <sup>a</sup>	2.0	254	1.180	2.59	0.015	0.085	0.007	0.040
B <sup>b</sup>	1.3	252	1.580	2.59	0.003	0.014	0.006	0.037
B	1.3	252	1.160	2.58	0.004	0.022	0.004	0.022
C <sup>c</sup>	2.4	252	1.155	2.59	0.006	0.035	0.008	0.047
B	5.0	252	1.020	2.59	0.016	0.091	0.022	0.125
B	1.1	216	9.00	19.4	0.030	0.180	0.14	0.841

<sup>a</sup>A: Designates  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixture in which  $\text{PuO}_2$  was obtained from  $\text{UO}_2$ - $\text{PuO}_2$  solid-solution pellets containing ~5 w/o plutonium. Pellets were oxidized to form  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$ , and additional  $\text{U}_3\text{O}_8$  was added to bring plutonium concentration to about 0.4 w/o.

<sup>b</sup>B: Designates  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixtures prepared by mechanically mixing  $\text{U}_3\text{O}_8$  and  $\text{PuO}_2$  to produce mixtures containing about 0.4 or 3.0 w/o plutonium.

<sup>c</sup>C: Designates  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixture prepared by oxidizing  $\text{UO}_2$ - $\text{PuO}_2$  solid-solution powder containing about 0.4 w/o plutonium.



on the alumina of 0.022 w/o, indicating that the low feed rate may be important. In the last experiment listed in Table IV, the  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$ -F.P. mixture contained about 3 w/o plutonium instead of the usual 0.4 w/o. This experiment resulted in a retention of 0.14 w/o plutonium on the alumina, indicating that the retention of plutonium is probably dependent on the quantity of plutonium fed to the reactor. Additional data on the effect of the quantity of plutonium fed to the alumina bed on the plutonium retention are presented in Table V.

TABLE V. Fluid-bed Fluorination of  $\text{PuO}_2$ : Effect of Quantity of Plutonium and Fission Products on Plutonium Retention on Alumina

Feeding-fluorination Period							
Temperature:		500°C					
Total gas flow rate:		12 liters/min (at room temp and 1.32 atm)					
Gas velocity:		0.98 ft/sec					
Fluorine concentration in total flow:		20 v/o					
Alumina in bed:		400 g					
Alumina in feed:		170 g					
Recycle-fluorination Period							
Recycle period:		550°C, 10 hr					
Total gas flow rate:		8 liters/min (at 1.32 atm)					
Linear velocity of gas phase:		0.71 ft/sec					
Fluorine concentration:		100%					
Analytical Results							
Exp. No.	Feed Material, g		Pu in Alumina Bed		Pu in Disengaging Chamber		Pu Volatilized, <sup>a</sup> %
	Pu	F.P.	w/o	g	w/o	g	
A. <u>Low Plutonium, Variable F.P.</u>							
1	1.23	None	0.0085	0.044	0.77	0.014	96
2	1.23	2.58 <sup>b</sup>	0.0048	0.027	0.31	0.008	98
3	1.23	19.4 <sup>b</sup>	0.014	0.080	0.09	0.010	93
4	1.23	19.4 <sup>b</sup>	0.025	0.148	0.59	0.027	88
B. <u>High Plutonium, Variable F.P.</u>							
5	9.24	None	0.12	0.632	2.70	0.052	93
6	9.18	2.58 <sup>b</sup>	0.19	1.100	22.8	0.802	88
7	9.13	14.9 <sup>c</sup>	0.71	4.340	13.9	0.483	53
8	9.13	14.9 <sup>c</sup>	0.71	4.409	-	-	52

<sup>a</sup>Based on plutonium retained in bed alone.

<sup>b</sup>F.P. mixture contained  $\text{MoO}_3$ . The F.P. mixture contained  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{ZrO}_2$ , and  $\text{MoO}_3$ . (For relative concentrations of the F.P. oxides, see Table II.)

<sup>c</sup>F.P. mixture did not contain  $\text{MoO}_3$ . Composition is that indicated in footnote b, less the  $\text{MoO}_3$ .

## 2. Effect of Added Bismuth

An investigation was made to determine the effect of adding bismuth metal, followed by refluorinating, on the plutonium content of an alumina bed that had been used for the fluorination of a  $U_3O_8$ - $PuO_2$ -F.P. mixture. Bismuth was added to the bed because it was believed that the fluorination product of bismuth,  $BiF_5$ , which is highly reactive,<sup>6</sup> might react with the plutonium residue, converting it to  $PuF_6$ . An alumina bed containing 0.18 w/o plutonium was chosen for these tests. One gram of bismuth was mixed with 50 g of the bed material. This mixture was then fed into 400 g of the bed material contained in the reactor at 550°C. This addition was followed by a recycle-fluorination of 5 hr at 550°C. After the first treatment, the alumina bed contained 0.08 w/o plutonium, less than one-half the original plutonium content. The second bismuth addition and fluorination cycle did not reduce the plutonium content of the alumina bed further. These results indicate that the presence of bismuth in the alumina bed will not materially assist in the removal of plutonium.

Supplementary to this investigation, the effect of the addition of  $BiF_3$  on the fluorination of  $U_3O_8$  and  $UO_2F_2$  was studied. The results are given in Appendix B of this report.

## 3. Effect of Quantity of Plutonium and Fission Products

Experiments were performed to investigate the effect of the quantities of plutonium and fission products fed to the reactor on the plutonium retention on alumina. These experiments were carried out with  $PuO_2$  or  $PuO_2$ -F.P. mixtures as the feed. A feeding-fluorination period at 500°C, with a gas phase containing 20 v/o fluorine in nitrogen, and a recycle-fluorination period of 10 hr at 550°C, using 100% fluorine, were employed. During the feeding-fluorination period, 150 g of 120-mesh alumina containing only  $PuO_2$  or a  $PuO_2$ -F.P. mixture was fed at a rate of from 3 to 6 g/min into the reactor containing 400 g of alumina. The experiments designated in Section A of Table V as "low plutonium" experiments used about 1.5 g of  $PuO_2$  containing about 1.2 g of plutonium; the corresponding quantity of the F.P. oxide mixture was 2.58 g. The ratio of plutonium to fission product as well as the quantity of plutonium are identical to those reported in Tables III and IV. The experiments designated in Section B of Table V as "high plutonium" experiments contained about 10.5 g of  $PuO_2$  containing about 9.2 g of plutonium. The quantity of fission products, 19.4 or 14.9, was dependent on whether the mixture contained  $MoO_3$ , the larger quantity being for the mixture containing  $MoO_3$ .\*

\*The presence of  $MoO_3$  in the F.P. mixture is believed to have contributed to plugging of valves in the cold-trapping system and hence was not used in some experiments. Analysis of solids removed from plugged valves showed the presence of molybdenum, plutonium, and bismuth. The bismuth was present as the result of experiments performed using that element to facilitate the removal of plutonium retained on alumina residues.

In Table V, Section A contains the data for the experiments with low plutonium content and variable F.P. content; Section B contains the data for the experiments with high plutonium content and variable F.P. content. For the experiments using small quantities of plutonium, an increase in the F.P. level from 2.58 to 19.4 g resulted in an increase in the plutonium retention on the alumina from 0.0048 w/o (Experiment 2) to 0.020 w/o (average of Experiments 3 and 4). For the high-plutonium experiments, the plutonium retention on the alumina was 0.12 for experiments in which fission products were not present, and 0.19 w/o for experiments in which fission products (2.58 g) were present. When the F.P. level was raised to 14.9 g, the plutonium retention on the alumina increased to 0.71 w/o. For a plutonium concentration of 0.4 w/o in the  $U_3O_8$ -PuO<sub>2</sub>-F.P. mixtures, the quantity of fission products was 2.58 g; for a plutonium level of 3 w/o in the  $U_3O_8$ -PuO<sub>2</sub>-F.P. mixture, the quantity of fission products was 19.4 or 14.9 g.

These results show a 20- to 50-fold increase in plutonium retention on the alumina for a 7.5-fold increase in the plutonium fed to the reactor for experiments in which fission products were not present (Experiments 1 and 5) and for the experiments in which the small quantities of fission products were present (Experiments 2 and 6). Increasing the F.P. level 7.5-fold resulted in an increase in plutonium retention on the alumina by a factor between three and four (Experiments 3 and 4 versus Experiment 2 for the tests with low levels of plutonium, and Experiments 7 and 8 versus Experiment 6 for the tests with high levels of plutonium).

#### 4. Effect of the Use of a Nonfluidized Static Bed

Several experiments were performed during which the alumina bed was not fluidized to determine if fluorination under static-bed conditions would result in efficient removal of plutonium. In these experiments, the solid charge of PuO<sub>2</sub> (1.4 g) and F.P. oxides (2.0 g, no MoO<sub>3</sub>) was mixed with 570 g of nominal 60-mesh alumina from which the -170 mesh fraction had been removed. This mixture was placed directly in the reactor rather than being fed into the bed. Three reaction periods were employed; the first at 450°C for 5 hr, the second at 500°C for 5 hr, and the third at 550°C for 10 hr. The gas phase contained 100% fluorine. The alumina bed after these reactions contained an average of 0.075 w/o plutonium. Comparable experiments in which a fluidized bed was used resulted in plutonium concentrations in the alumina of from 0.002 to 0.004 w/o (see Table VI). These results indicate that the use of a static-bed fluorination technique under these conditions would not result in adequate removal of plutonium.

TABLE VI. Fluid-bed Fluorination of  $\text{PuO}_2$ -F.P. Mixtures: Effect of Fluorine Flow Rate on Plutonium Retention on Alumina

Solid charge to reactor:	1.4 g of $\text{PuO}_2$ (1.25 g of Pu) 2.0 g of F.P. oxide mixture <sup>a</sup> 570 g of 60-mesh Alumina (+170) <sup>b</sup>
Gas phase:	100% fluorine
Recycle-fluorination periods:	(1) 450°C, 5 hr; (2) 500°C, 5 hr; (3) 550°C, 10 hr

Fluorine Flow Rate, liters/min	Linear Velocity, ft/sec (500°C, 1.32 atm)	Pu Concentration in $\text{Al}_2\text{O}_3$		Pu Volatilized, %
		w/o	g	
4	0.33	0.026	0.148	88.2
4	0.33	0.019	0.108	91.4
6	0.49	0.0033	0.022	98.2
7	0.57	0.0038	0.022	98.2
8	0.67	0.0022	0.013	99.0
8 <sup>c</sup>	0.67	0.0022	0.013	98.0

<sup>a</sup>The F.P. mixture contains the following oxides:  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{BaO}$ , and  $\text{ZrO}_2$ . See Table II for quantity of each oxide in mixture.

<sup>b</sup>Nominal 60 mesh (manufacturer's designation) from which -170 mesh fraction had been removed.

<sup>c</sup>Solid reaction charge contained 0.63 g of plutonium.

##### 5. Effect of Fluorinating Gas Flow Rate

A series of experiments was performed to determine the effect of fluorinating gas flow rate on the plutonium retention in the alumina bed. These experiments employed the same quantities of solid reaction charge used in the static-bed experiments. The gas phase of 100% fluorine was recycled through the alumina bed at flow rates from 4 to 8 liters/min. The results obtained for these experiments are listed in Table VI. At a gas flow rate of 4 liters/min, the plutonium concentration in the alumina bed averaged 0.022 w/o; at gas flow rates of 6 to 8 liters/min, the plutonium content of the alumina bed ranged from 0.002 to 0.004 w/o. These results indicate that a gas flow rate of 6 liters/min (linear velocity of 0.49 ft/sec at 500°C) or greater is necessary for effective removal of plutonium from the alumina bed.

## 6. Effect of Type of Alumina Used

The plutonium retention on two mesh sizes of Type RR (high-purity) alumina, nominal 120 and 60 mesh, can be compared from data in this report. In Table V, experiments are reported using 120-mesh alumina. Fluorination for 10 hr at 550°C resulted in a residual plutonium concentration on the alumina of 0.005 w/o (Table V, Experiment No. 2, Section A). Experiments are reported in Table VI using 60-mesh alumina. After a fluorination series of 5 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C, the plutonium concentration on the alumina was 0.002 w/o. Considering the longer fluorination time for the experiment listed in Table VI, these data probably indicate similar plutonium retentions on the two types of alumina.

Presently, Alcoa Type T-61 alumina is being used in pilot-scale tests in place of the high-purity Type RR alumina previously used. The use of Type T-61 alumina would result in lowered cost for the fluid-bed material. One experiment was performed using the same solid reaction charge and reaction conditions as for the experiments listed in Table VI. The fluorine flow rate was 8 liters/min, corresponding to a linear velocity of 0.67 ft/sec at 500°C. After fluorination, the alumina bed contained 0.0026 w/o plutonium. This result corresponds to those obtained, under the same reaction conditions, using the high-purity Type RR alumina and indicates that Type T-61 alumina is as suitable as the Type RR previously employed.

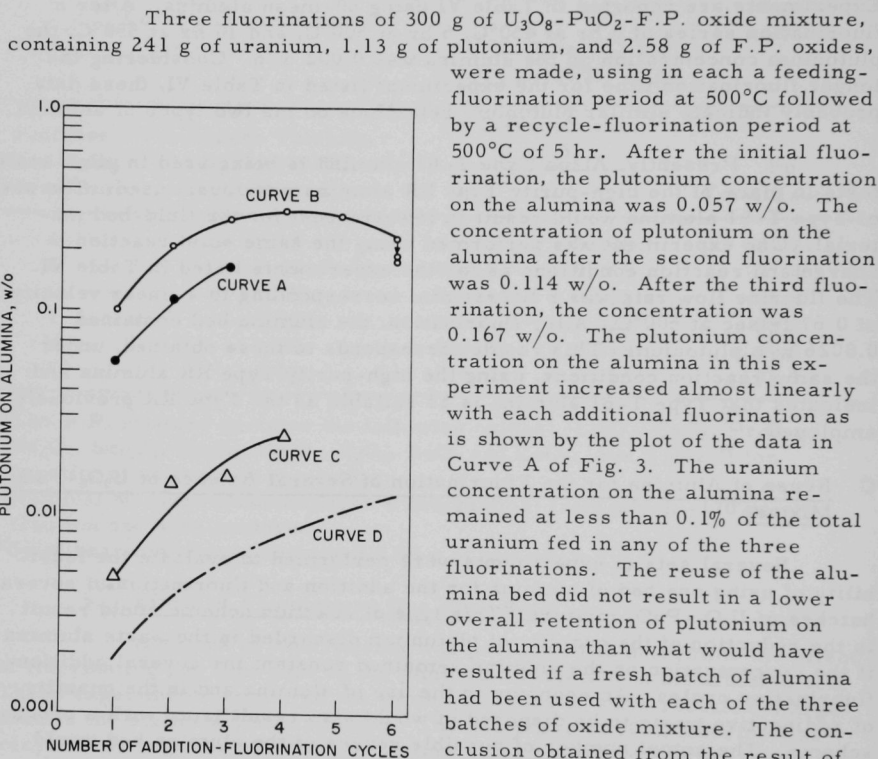
## C. Reuse of Alumina for the Fluorination of Several Batches of $U_3O_8$ -PuO<sub>2</sub> Mixture

Several sets of experiments were performed to evaluate the feasibility of using one bed of alumina for the addition and fluorination of several batches of  $U_3O_8$ -PuO<sub>2</sub> mixture. This type of reaction scheme could result in the reduction of the quantity of plutonium discarded in the waste alumina if the concentration on the alumina remained constant for several addition-fluorination cycles. An economy in the use of alumina and in the quantity of radioactive waste to be disposed of would also result from such a process scheme. The actual number of possible reuses of the alumina bed would mainly depend on the heat loading of the alumina bed due to the accumulation of fission products. No firm estimate of this number has as yet been made.

The general procedure for these experiments was as follows: In each addition, 300 g of  $U_3O_8$ -PuO<sub>2</sub>-F.P. mixture, or about 2.0 g of PuO<sub>2</sub>-F.P. mixture, blended with 150 g of alumina, was fed into a 400-g alumina bed in the reactor and there contacted with a gas phase containing 20 v/o fluorine and 80 v/o nitrogen. Following the feeding-fluorination period, the fluorination was continued with one or more recycle-fluorination periods using 100% fluorine at 450, 500, and 550°C. The alumina bed was removed

from the reactor after each addition-fluorination cycle and sampled; then it was split into two portions, 400 g to be replaced in the reactor, and 150 g to be mixed with the next feed charge. In one set of experiments the alumina bed was removed, sampled, and partitioned after each feeding-fluorination cycle and only one final recycle-fluorination cycle was used.

### 1. Reuse Experiment, Set 1



- Curve A: Reuse Experiment, Set 1  
 Curve B: Reuse Experiment, Set 2  
 Curve C: Reuse Experiment, Set 3  
 Curve D: Theoretical plutonium concentration on alumina corresponding to removal of 99% of total plutonium fed to the reactor

Fig. 3. Effect of the Reuse of Alumina Fluid Bed for Several Additions and Fluorinations on the Plutonium Retention on the Alumina

Three fluorinations of 300 g of  $U_3O_8$ - $PuO_2$ -F.P. oxide mixture, containing 241 g of uranium, 1.13 g of plutonium, and 2.58 g of F.P. oxides, were made, using in each a feeding-fluorination period at 500°C followed by a recycle-fluorination period at 500°C of 5 hr. After the initial fluorination, the plutonium concentration on the alumina was 0.057 w/o. The concentration of plutonium on the alumina after the second fluorination was 0.114 w/o. After the third fluorination, the concentration was 0.167 w/o. The plutonium concentration on the alumina in this experiment increased almost linearly with each additional fluorination as is shown by the plot of the data in Curve A of Fig. 3. The uranium concentration on the alumina remained at less than 0.1% of the total uranium fed in any of the three fluorinations. The reuse of the alumina bed did not result in a lower overall retention of plutonium on the alumina than what would have resulted if a fresh batch of alumina had been used with each of the three batches of oxide mixture. The conclusion obtained from the result of this fluid-bed fluorination experiment is identical to that for a similar experiment performed using the boat reactor (Reference 2, page 13).

### 2. Reuse Experiment, Set 2

In this alumina reuse experiment, six additions of 300 g of  $U_3O_8$ - $PuO_2$ -F.P. oxide mixture



(each containing about 250 g of U, 1.16 g of Pu, and 2.58 g of F.P.) mixed with 150 g of alumina were made to one alumina bed. The six feeding-fluorination periods were performed consecutively at 500°C and then followed by recycle-fluorination periods of 10 hr at 500°C and 10 hr at 550°C. The feed rate during these experiments was about 5 g of  $U_3O_8$  per minute. After each feeding-fluorination period, the bed was removed from the reactor and split into two parts as described previously to supply the next bed and the alumina for the next feed mixture. This alumina reuse procedure was employed to determine if the total reaction time could be shortened by using only one recycle-fluorination period to remove the accumulated plutonium from the alumina bed.

Analyses of samples of the alumina beds following the feeding-fluorination periods showed that the concentration of plutonium on the alumina increased rather regularly (from 0.10 to 0.30 w/o) for the first four additions of  $U_3O_8$ -PuO<sub>2</sub>-F.P., and then decreased to a value of 0.23 w/o after the sixth addition. These data are shown as Curve B of Fig. 3. The uranium concentration on the alumina varied rather widely from 0.16 to 2.0 w/o, and after the sixth addition the uranium concentration was 0.64 w/o. Uranium and plutonium concentrations on the alumina after the 10-hr, 500°C, recycle-fluorination period were 0.13 and 0.19 w/o, respectively; after the 10-hr, 550°C recycle-fluorination they were 0.01 and 0.18 w/o, respectively. This level of plutonium on the alumina represents 14% of the total plutonium fed to the bed (6.98 g), corresponding to volatilization of 86% of the plutonium as the hexafluoride. The 0.01 w/o uranium on the alumina bed corresponds to removal of more than 99.9% of the total uranium fed to the bed (1510 g).

For comparison, a single experiment using a feeding-fluorination period at 500°C and recycle-fluorination period at 550°C of 15 hr (Table III, Section B, entry 3) resulted in removal of 85% of the plutonium and about 99.9% of the uranium. Six experiments of this type would then result in identical conversions of plutonium and uranium to the hexafluorides, as was found for this reuse experiment. This type of reuse procedure would therefore result in economy in alumina use, in quantity of waste disposal, and in total reaction time (a reduction in time of about 70 hr); however, the 85% level of plutonium removal in this experiment is far below the 99% plutonium removal desired.

### 3. Reuse Experiment, Set 3

A reuse experiment was performed in which only a PuO<sub>2</sub>-F.P. oxide mixture blended with alumina was fed into the bed. Four additions were made, and each feed mixture contained about 1.2 g of plutonium and 2.6 g of fission products. For each PuO<sub>2</sub>-F.P. addition, a feeding-fluorination period was conducted at 500°C followed by a recycle-fluorination period at 550°C for 10 hr.

The progress of plutonium removal, as shown in Curve C of Fig. 3, indicates that the plutonium concentration on the alumina was 0.0048 w/o after the first addition of  $\text{PuO}_2$ -F.P. mixture, rose to 0.014 w/o after the second addition, and remained near this level for the subsequent two additions, 0.015 and 0.025 w/o. If the plutonium concentration on the alumina were to remain at this level ( $\sim 0.02$  w/o) for a series of seven additions to a single bed, then the plutonium retained on the alumina would represent only 1% of the total plutonium fed to the reactor.

The reaction conditions used in this set of experiments represent the plutonium cleanup recycle-fluorination for an experiment of the type listed as the last entry in Section B of Table III. The cited experiment, which used a feeding-fluorination period at  $450^\circ\text{C}$ , followed by recycle-fluorination periods of 5 hr at  $450^\circ\text{C}$ , 5 hr at  $500^\circ\text{C}$ , and 10 hr at  $550^\circ\text{C}$ , resulted in concentrations of plutonium and uranium in the alumina bed of 0.007 and 0.015 w/o, respectively. This suggests that alumina-reuse series using these reaction conditions would result in low concentrations of both plutonium and uranium in the final alumina bed. Such a set of experiments is reported in Set 4 of the reuse experiments (immediately following).

#### 4. Reuse Experiment, Set 4

In this series of reuse experiments, in which the reaction conditions suggested by the previously described experiments were used, the effect of the presence of  $\text{MoO}_3$  in the F.P. mixture on the plutonium retention on alumina was also investigated. Cold-trap manifold valves were plugged by a solid containing both molybdenum and plutonium during the course of this work (cf. footnote on page 20); this fact suggested a possible interaction between molybdenum and plutonium compounds, which might result in the production of a nonvolatile plutonium-containing compound. Therefore, two series of experiments were performed in as nearly an identical manner as possible to evaluate the effect of molybdenum on plutonium retention. In one series, the F.P. mixture did not contain  $\text{MoO}_3$ ; in the second series, it did contain  $\text{MoO}_3$ . The composition of the F.P. mixtures is shown in Table II. In addition, in one series of experiments (those in which the F.P. mixture contained  $\text{MoO}_3$ ), the alumina bed was analyzed for fluoride content and the surface area was also measured after each addition cycle. This was done to obtain an indication of the attrition of the fluid-bed alumina with repeated use.

The procedure for these experiments was as follows: in each addition, 300 g of  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$ -F.P. mixture blended with 150 g of 120-mesh alumina was injected into the 400-g alumina bed at  $450^\circ\text{C}$  and there contacted with dilute fluorine. Following the feeding-fluorination period, the fluorination was continued for three recycle-fluorination periods: the first at  $450^\circ\text{C}$  for 5 hr, the second at  $500^\circ\text{C}$  for 5 hr, and the third at  $550^\circ\text{C}$  for

10 hr. In each experiment, 20 g of fresh alumina was added through the powder feeder at the end of the feeding-fluorination period as a wash for the feed line. At the end of each addition-fluorination cycle, the alumina bed, which weighed about 570 g, was removed from the reactor and sampled. Analyses for plutonium, uranium, fluoride, and surface-area determination were carried out. About 1 g of solids remained in the disengaging chamber of the reactor and was removed by rapping the outer wall of the chamber; this residue was returned to the bed for subsequent fluorination. The alumina bed was then divided into two parts: 400 g for the bed of the next experiment, and 150 g for mixing with 300 g of the  $U_3O_8$ -PuO<sub>2</sub>-F.P. mixture to make up the next feed material.

The data obtained and the experimental conditions used in these experiments are listed in Table VII and are shown in the plots of Fig. 4. The results for the reuse series in which the F.P. mixture did not contain MoO<sub>3</sub> are listed in Section A of Table VII. For addition-fluorination Cycles 1 through 7, the  $U_3O_8$ -PuO<sub>2</sub>-F.P. mixture contained about 0.4 w/o plutonium; for addition-fluorination Cycle 8, the  $U_3O_8$ -PuO<sub>2</sub>-F.P. mixture contained about 3 w/o plutonium. The F.P. content in the last addition was also raised proportionately. In Section B of Table VII, the F.P. mixture contained MoO<sub>3</sub>, and for all of these cycles, the  $U_3O_8$ -PuO<sub>2</sub>-F.P. mixture contained about 0.4 w/o plutonium.

The results obtained for the reuse series in which the F.P. mixture did not contain MoO<sub>3</sub> (Section A of Table VII and Curve A of Fig. 4) showed 0.0046 w/o plutonium in the alumina after the first addition-fluorination cycle and 0.0036 w/o plutonium in the alumina after the second addition-fluorination cycle. These values of plutonium retention on the alumina corresponded to volatilization of 97.4 and 99.0% of the total plutonium charged to the reactor, respectively. After the third addition-fluorination cycle, the alumina bed contained 0.193 w/o plutonium. This high level of retention was considered to be due to malfunctioning of the reactor-filter blow-back system. The high level of plutonium in the alumina bed was reduced by subsequent addition-fluorination cycles, and after the fifth cycle the plutonium content of the alumina was 0.010 w/o, corresponding to volatilization of 99% of the plutonium. After the eighth cycle, during which the quantity of plutonium fed to the reactor was more than doubled, the plutonium content of the alumina bed was 0.025 w/o, corresponding to volatilization of 99.2% of the total plutonium fed to the reactor.

The results for the alumina-reuse series in which the F.P. mixture contained MoO<sub>3</sub> are listed in Section B of Table VII and presented as Curve B of Fig. 4. After the first addition-fluorination cycle, the alumina bed contained 0.003 w/o plutonium. The concentration of plutonium in the alumina rose to 0.03 w/o after the second addition-fluorination cycle\*

\* This large increase in plutonium concentration on the alumina was probably due to the same condition that caused a similar increase in the plutonium content on the alumina for the set of experiments described in Section A of Table VII.

TABLE VII. Fluid-bed Fluorination of  $U_3O_8$ -PuO<sub>2</sub>-F.P. Mixtures: Effect of the Reuse of Alumina for Several Additions and Fluorinations on Plutonium Retention on Alumina

Feeding-fluorination Period									
Temperature:					450°C				
Total gas flow rate:					12 liters/min (0.79 ft/sec)				
Fluorine concentration in total flow:					20 v/o				
Alumina in bed:					400 g (120 mesh)				
Alumina in feed material:					150 g (+20 g wash, 120 mesh)				
Recycle-fluorination Period									
Recycle periods:					(1) 450°C, 5 hr; (2) 500°C, 5 hr; (3) 550°C, 10 hr				
Total gas flow rate:					8 liters/min (0.67 ft/sec at 500°C)				
Fluorine concentration:					100%				
Addition- fluorination Cycle	Feed Material, <sup>a</sup> g			U <sub>3</sub> O <sub>8</sub> -PuO <sub>2</sub> Feed Rate, g/min	Concentration in Al <sub>2</sub> O <sub>3</sub> Bed				Pu Volatilized, <sup>b</sup> %
	Pu	U	F.P.		Pu		U		
					w/o	g	w/o	g	
A. Experiments in Which F.P. Mixture Did Not Contain MoO <sub>3</sub> <sup>c</sup>									
1	0.986 (0.986) <sup>d</sup>	250	1.99	1.6	0.0046	0.026	0.010	0.057	97.4
2	1.182 (2.168)	254	2.56	3.3	0.0036	0.021	0.009	0.051	99.0
3	1.182 (3.350)	254	2.56	2.2	0.193	1.175	3.60	21.92	65.0
4	1.162 (4.512)	248	2.54	1.8	0.012	0.070	0.042	0.245	98.4
5	1.198 (5.710)	254	2.60	2.2	0.010	0.058	0.039	0.226	99.0
6	1.194 (6.904)	254	2.60	1.5	0.0093	0.054	0.025	0.145	99.2
7	1.223 (8.127)	256	2.60	1.5	0.0088	0.051	0.043	0.250	99.4
8	8.647 (16.774)	234	16.00	1.1	0.025	0.150	0.004	0.024	99.2
B. Experiments in Which F.P. Mixture Contained MoO <sub>3</sub> <sup>e</sup>									
1	0.990 (0.990) <sup>d</sup>	254	2.58	2.22	0.003	0.017	0.009	0.052	98.3
2	1.209 (2.199)	254	2.58	2.27	0.030	0.171	0.006	0.034	92.2
3	1.213 (3.412)	254	2.58	2.25	0.028	0.161	0.105	0.604	95.3
4	1.225 (4.637)	257	2.62	2.30	0.018	0.105	0.070	0.403	97.7
5	1.218 (5.855)	254	2.58	2.50	0.014	0.082	0.005	0.028	98.6

<sup>a</sup>Composed of about 300 g of a  $U_3O_8$ -PuO<sub>2</sub>-F.P. mixture containing about 0.4 w/o Pu, 84 w/o U, and 0.85 w/o F.P. oxides (for the quantity of the individual oxides in the F.P. oxide mixture see Table II) mixed with 150 g of nominal 120-mesh alumina.

<sup>b</sup>Based on the quantity of plutonium retained in the alumina bed and that fed to the fluid-bed reactor.

<sup>c</sup>The F.P. mixture contained the following oxides: La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Pr<sub>6</sub>O<sub>11</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, BaO, and ZrO<sub>2</sub>.

<sup>d</sup>Figures in parentheses are the cumulative quantity of plutonium fed to the fluid-bed reactor.

<sup>e</sup>The F.P. mixture contained those oxides listed in footnote c plus MoO<sub>3</sub>.

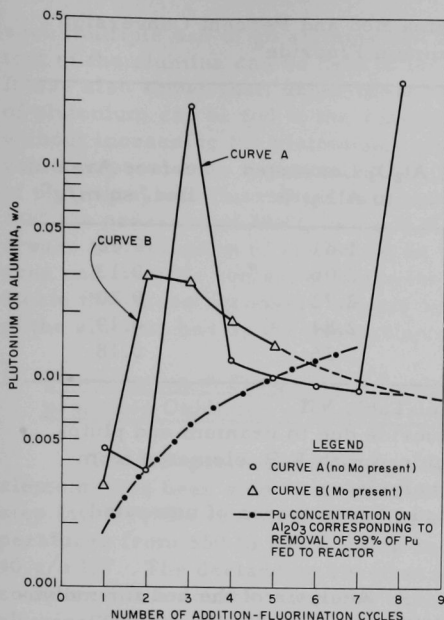


Fig. 4. Effect of the Reuse of Alumina Bed for Several Additions and Fluorinations and of the Presence of Molybdenum in the F.P. Mixture on the Plutonium Retention on the Alumina. (For listing of data, see Table VII.)

and then decreased gradually to a value of 0.014 w/o after the fifth addition-fluorination cycle. The concentration of 0.014 w/o plutonium on the alumina after the fifth and last addition-fluorination cycle corresponded to volatilization of greater than 98% of the plutonium charged to the reactor. If the plutonium level of the alumina bed remained at 0.014 w/o for two additional addition-fluorination cycles, then the alumina would contain 1% or less of the plutonium charged to the reactor. These results do not show a significant increase in plutonium retention on the alumina due to the presence of  $MoO_3$  in the F.P. mixture.

If the system malfunction that caused the greater plutonium retention on certain addition-fluorination cycles had not occurred, it is probable that in both series of experiments the plutonium concentration on the alumina would have achieved suitably low values after only two or three addition-fluorination cycles. The plots of Fig. 4 show that, for the experi-

ments in which the F.P. mixture did not contain molybdenum, the plutonium concentration on the alumina was at the desired level after the second addition-fluorination cycle. Further, the plots after the fourth addition-fluorination cycle for Curve A, and after the third addition-fluorination cycle for Curve B, show the similar change in the plutonium concentration on the alumina with subsequent cycles for the two sets of experiments.

The fluoride content and surface area of the alumina bed, listed in Table VIII and shown in Fig. 5, were determined after each addition-fluorination cycle for the series of experiments listed in Section B of Table VII. The fluoride content of the alumina bed showed an average increase of about 0.5% per addition-fluorination cycle following the 1.4% level reached after the first addition-fluorination cycle. Surface-area measurements by the BET method showed a value of 0.08 sq m/g after the first addition-fluorination cycle,\* rising to a value of 0.13 sq m/g after the second addition-fluorination. The surface area was 0.20 sq m/g after the third cycle and remained relatively constant for the fourth and fifth cycles.

\*Original surface area of the 120-mesh alumina was 0.011 sq m/g.

TABLE VIII. Surface Area of Alumina Bed and Percent Conversion of Alumina to Aluminum Fluoride<sup>a</sup>

Addition-fluorination Cycle	Fluoride Analysis of Alumina			Al <sub>2</sub> O <sub>3</sub> Converted to AlF <sub>3</sub> , %	Surface Area of Bed, sq m/g <sup>c</sup>
	F, %	Total F, g	F as <sup>b</sup> AlF <sub>3</sub> , g		
1	1.74	10.02	8.95	1.41	0.08
2	2.68	15.30	13.13	2.06	0.13
3	3.60	20.74	17.34	2.72	0.20
4	3.90	22.46	18.09	2.84	0.19
5	4.60	26.08	20.78	3.26	0.18

<sup>a</sup>For experiments listed in Section B of Table VII.

<sup>b</sup>This value obtained by subtracting fluoride due to uranium and plutonium content of bed and fluoride combined with F.P. elements from the total fluoride as determined by analysis.

<sup>c</sup>Surface areas obtained by BET method. Surface area of untreated 120-mesh alumina is 0.011 sq m/g.

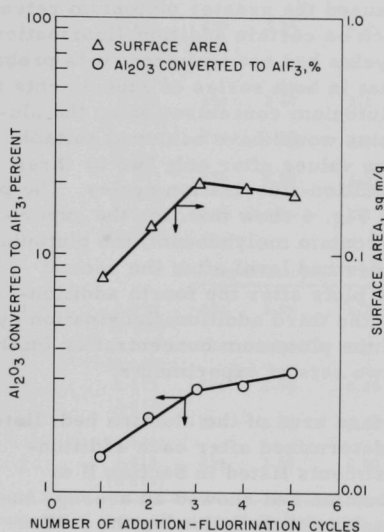


Fig. 5. Change in Surface Area and Conversion of Alumina to AlF<sub>3</sub> as a Function of Reuse Cycles of an Alumina Bed. (For listing of data, see Table VIII.)

Analysis of the bed for molybdenum after the second addition-fluorination cycle (Table VII, Section B) indicated that less than 3% of the molybdenum fed to the reactor remained in the alumina bed. The analysis, carried out by a colorimetric method, indicated the molybdenum content of the bed to be less than 0.004 w/o. It is likely that the molybdenum content of the bed is actually significantly less than 0.004 w/o since an X-ray fluorescence scan of a sample of the bed (purported to be sensitive to concentrations of molybdenum in the ppm range) showed no detectable molybdenum. For comparison, it may be noted that one addition of the F.P. mixture would result in a residual concentration of 0.06 w/o molybdenum in the bed if none of the molybdenum was removed from the bed.

The results obtained in these alumina-reuse experiments show that



such multiple use of an alumina bed is feasible and that the plutonium content of the alumina can be held to less than 1% of that fed to the reactor. It was also shown that, under these reaction conditions, larger quantities of plutonium can be fed to the reactor (Cycle 8, Section A of Table VII) without increasing the plutonium content of the alumina to an excessive value as previously experienced (cf. last entry, Table IV) when this amount of plutonium was fluorinated in a new alumina bed. These data also show that the presence of  $\text{MoO}_3$  in the F.P. mixture does not materially increase the retention of plutonium on the alumina. Finally, the surface area and fluoride content data for the alumina bed (Table VIII, Fig. 5) indicate that these secondary effects would not seriously hamper the reuse of the alumina bed by the production and accumulation of fines.

D. Fluorination of Simulated Reaction Products Resulting from HF-promoted Oxidation of Stainless-steel-clad Uranium Dioxide Fuel

The HF-promoted oxidative decladding of stainless-steel-clad fuel elements has been studied at BNL<sup>7</sup> and at ORNL and ANL.<sup>8</sup> This process step involves the chemical destruction of the cladding by reaction at temperatures from 550 to 650°C using an oxygen-HF mixture containing 40 v/o HF. The decladding reaction would result in the formation of a considerable amount of iron and chromium oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ) in the alumina bed, in addition to uranium and plutonium fluorides and oxyfluorides. As much as 5 to 10% of the resulting alumina bed would be composed of iron and chromium oxides. Experiments were performed to determine if the presence of the decladding products would affect the plutonium retention in the alumina bed.

The use of the HF-promoted oxidation step would result in an alumina bed containing the decladding product and fuel-element components dispersed throughout the alumina. For these experiments, the solid reaction charge containing  $\text{PuF}_4$ ,  $\text{UO}_2\text{F}_2$ , F.P. fluorides, stainless-steel-decladding product, and Type T-61 alumina was placed in the reactor and fluorinated. During the initial fluorination carried out for about 1 hr, the gas phase contained 5 to 20 v/o fluorine in nitrogen and the reaction temperature was 450°C. During this portion of the reaction, the gas phase was passed through a series of cold traps to remove the  $\text{UF}_6$  and  $\text{PuF}_6$ . The uncondensed gases were then passed through an activated alumina trap to dispose of the fluorine, and the nitrogen was vented to the box atmosphere. After the initial reaction period, the system was put on recycle and the gas phase was changed to 100% fluorine. During the recycle period, the gas phase was passed from the reactor through the cold traps to remove  $\text{UF}_6$  and  $\text{PuF}_6$  and then returned to the reactor by means of the Lapp pump. The recycle periods were 4 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C. Samples of the starting material and the bed remaining after the experiment were taken and analyzed for uranium and plutonium content to allow

calculation of the degree of removal affected by the fluorination treatment. Three experiments were performed, the third experiment involved a further addition of the solid reaction charge to the alumina bed used for the second experiment.

The quantities of materials in the solid charge, the reaction conditions, and the results obtained for these experiments are listed in Table IX. For the two single addition-fluorination experiments, the alumina beds contained 0.0087 and 0.010 w/o plutonium and 0.041 and 0.012 w/o uranium, respectively. The data listed for the last entry in Table IX are for the second addition-fluorination to the alumina bed resulting from the second experiment listed in Table IX. The plutonium and uranium concentrations in the alumina bed after this experiment were 0.014 and 0.033 w/o, respectively. This modest increase in plutonium concentration on the alumina indicates that multiple use of an alumina bed for this type of solid charge could be successfully accomplished.

TABLE IX. Fluid-bed Fluorinations of  $\text{UO}_2\text{F}_2$ ,  $\text{PuF}_4$ , F.P. Fluoride, and Stainless-steel-decladding Product Mixtures

Fluorination Periods											
1st period:						450°C, 1 hr, 5-20% F <sub>2</sub>					
						4 hr, 100% F <sub>2</sub>					
2nd period:						5 hr, 500°C, 100% F <sub>2</sub>					
3rd period:						10 hr, 500°C, 100% F <sub>2</sub>					
Gas flow rate:						8 liters/min (at 1.32 atm)					
Linear velocity of gas phase:						0.67 ft/sec (at 500°C)					
Feed Material, <sup>a</sup> g						Concentration in Al <sub>2</sub> O <sub>3</sub> Bed					
Exp. No.	Pu		U	F.P. <sup>b</sup>	S.S.-declad Product <sup>c</sup>	Al <sub>2</sub> O <sub>3</sub> <sup>d</sup>	Pu		U		Volatilized, <sup>e</sup> %
							w/o	g	w/o	g	
1	1.252	254	2.28	45.0	570	0.0087	0.053	0.041	0.240	95.8	
2a	0.943	191	1.71	33.8	428	0.010	0.048	0.012	0.056	94.9	
2b	0.943	191	1.71	45.0	455	0.014	0.069	0.033	0.165	96.3	
	(1.886) <sup>f</sup>										

<sup>a</sup>Mixture of  $\text{PuF}_4$ ,  $\text{UO}_2\text{F}_2$ , F.P. fluorides, stainless-steel-decladding products, and alumina.

<sup>b</sup>Prepared by fluorination of a mixture of 10 oxides (see note a, Table VI).

<sup>c</sup>Prepared by the  $\text{HF-O}_2$  reaction with Type 304 stainless steel.

<sup>d</sup>Type T-61 alumina having a median particle size of about 150 microns and a particle-size range of 80 to 250 microns.

<sup>e</sup>Based on plutonium remaining in alumina bed and total quantity of plutonium fed to reactor.

<sup>f</sup>Cumulative plutonium added in Experiments 2a and 2b.

A material balance was made for iron and chromium for an experiment of the type described above. In this experiment, a mixture containing 1.6 g of  $\text{PuF}_4$ , 300 g of  $\text{UO}_2\text{F}_2$ , 2.3 g of F.P. fluorides, 33 g of stainless-steel-decladding product, and 430 g of alumina was fluorinated for 20 hr at temperatures between 450 and 550°C. The stainless-steel-decladding product, prepared by the HF-promoted oxidation of Type 304 stainless steel, was analyzed and shown to contain, as major constituents, 47.6% iron and 12.8% chromium.

The distribution of iron and chromium in the reactor system for such a typical experiment is shown on the diagram of the reactor system in Fig. 6. The largest amount of iron (96%) remained in the alumina bed of the reactor, and 3% was found in the disengaging-chamber residue. However, only 35% of the chromium remained in the alumina bed, 2% appearing in the disengaging-chamber residue. The weights of the alumina bed and the disengaging-chamber residue were 467 and 1.9 g, respectively. A small amount of chromium (about 1%) was found in the outside filter chamber upstream of the reactor. These data indicate that a substantial portion of the chromium initially present in the reaction system will be transferred along with the volatile  $\text{UF}_6$  and  $\text{PuF}_6$ .

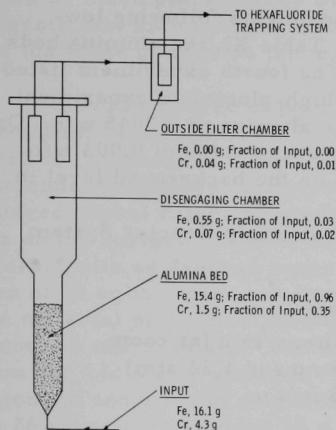


Fig. 6. Typical Distribution of Iron and Chromium in Fluid-bed Reactor System. (For experiments of the type described in Table IX.)

corresponded in volatility and color to that observed is chromyl fluoride ( $\text{CrO}_2\text{F}_2$ ). Attempts to identify this material by infrared absorption analysis were not successful. However, workers at BNL<sup>9</sup> observed this same material during the fluorination of stainless-steel-decladding product and were able to identify it as  $\text{CrO}_2\text{F}_2$  by means of infrared analysis.

#### E. Determination of Residual Plutonium in Reactor System

A series of blank experiments was performed to determine the extent of retention of plutonium in the fluid-bed reactor. These experiments were performed to determine the contribution by plutonium retained on the reactor surfaces to the plutonium-concentration levels on the alumina obtained during regular experiments. Some of these blank experiments were carried out after regular experiments had been completed using high levels of plutonium (9 g), and some were carried out after experiments had been completed using low levels of plutonium (1.2 g). One experiment was carried out after new disengaging-chamber filters, a new cold-trapping manifold, and new cold traps were installed. For these blank experiments, a short feeding-fluorination period at 500°C was used during which 170 g of alumina was fed into the 400-g alumina bed, followed by a recycle-fluorination period of 10 hr at 550°C.

The results obtained and the reaction conditions used for these experiments are listed in Table X. For the "clean" reaction system (Experiment 1, Table X), the alumina bed contained 0.0007 w/o plutonium, which can be considered to be the lowest level of plutonium likely to be observed in the reactor system. For the two blank experiments following low-plutonium experiments (Experiments 2 and 3, Table X), the alumina beds contained 0.0015 and 0.0055 w/o plutonium. The fourth experiment listed in Table X, which was performed following a high-plutonium experiment, resulted in a concentration of plutonium on the alumina of 0.0045 w/o. On the basis of these results it appears that an average value of 0.003 w/o plutonium on the alumina could be considered as the background level in

TABLE X. Determination of Residual Plutonium in Reactor System

<u>Feeding-fluorination Period</u>					
Temperature:		500°C			
Total gas flow:		12 liters/min (at room temp and 1.32 atm)			
Linear velocity:		0.98 ft/sec			
Fluorine concentration in total flow:		20 v/o			
Alumina in bed:		400 g			
Alumina in feed:		170 g			
<u>Recycle-fluorination Period</u>					
Recycle period:		550°C, 10 hr			
Total gas flow rate:		8 liters/min (at 1.32 atm)			
Linear velocity of gas phase:		0.71 ft/sec			
Fluorine concentration:		100%			
		<u>Analytical Results</u>			
Blank Exp. No.	Previous History of Reactor	<u>Pu in Alumina Bed</u>		<u>Pu in Disengaging Chamber</u>	
		w/o	g	w/o	g
1	"Clean" <sup>a</sup>	0.0007	0.004	0.50	0.006
2	Low Pu <sup>b</sup>	0.0015	0.011	0.32	0.006
3	Low Pu <sup>b</sup>	0.0055	0.033	0.24	0.017
4	High Pu <sup>c</sup>	0.0045	0.028	0.32	0.060

<sup>a</sup>Before this experiment, new disengaging chamber filters, new cold traps, and a new cold-trap manifold had been installed.

<sup>b</sup>Before this experiment, an experiment had been performed using 1.2 g of plutonium in feed charge.

<sup>c</sup>Before this experiment, an experiment had been performed using 9 g of plutonium in feed charge.

the  $1\frac{1}{2}$ -in.-diam reaction system. Also listed in Table X are the plutonium contents of the alumina residues retained on the walls of the disengaging chamber. These results show that the disengaging-chamber residues contained as much plutonium as was contained in the alumina bed. This fact suggests that the principal source of this residual plutonium in the system was the loose powder on the walls and filters of the disengaging chamber.

Another source of plutonium holdup in the reactor system is the permanent cake formed on the disengaging-chamber filters. This cake, which is composed of fines from the fluid-bed alumina and uranium and plutonium compounds, improves the filtering characteristics of the sintered-nickel filters by producing a more uniform pore-size distribution on the surface of the filter. Two 6-in.-long, sintered-nickel, bayonet filters,\* with an average pores size of  $10\ \mu$  and with a total active surface area of 30 sq in., were removed from the reactor after 26 experiments. The material on the surfaces of the filters was removed and analyzed for plutonium and uranium. The analysis showed a total of 2.6 mg of plutonium and 132 mg of uranium. These quantities represent 0.09 mg of plutonium and 4 mg of uranium per square inch of filter surface. During the 26 experiments, about 26 g of plutonium hexafluoride passed through these filters at approximately  $200^{\circ}\text{C}$ . Therefore, about  $3.5 \times 10^{-3}$  mg of plutonium was retained per square inch of filter surface per gram of  $\text{PuF}_6$  through the filters.

#### F. Autoradiography of Plutonium Contained on the Alumina

It is important to establish whether the plutonium is located on the surface of the alumina particles or dispersed throughout the body of the particle; this information is needed to guide further efforts toward lowering the retention of plutonium on alumina or devising means of removing the plutonium retained on the alumina. Autoradiographic experiments were performed to determine the location of the plutonium retained on the alumina of fluorinated fluid beds. The autoradiographic method, using the alpha activity of the plutonium to indicate the location of the plutonium on (or in) the alumina particles, was chosen as the experimental method. Adams and Steunenberg<sup>10</sup> showed that the site of plutonium in a metal matrix can be located by this method. The tracks developed by the alpha particles in a photographic emulsion are readily distinguishable from the general darkening produced by beta radiation.

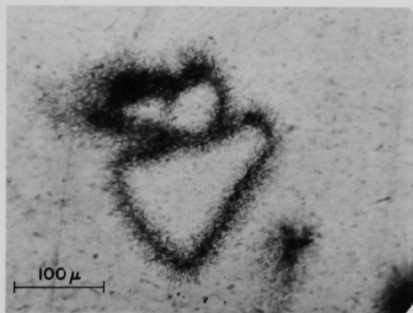
The alumina from two fluid beds was chosen for this work. One bed contained 0.12 w/o plutonium on the alumina, the second bed contained 0.005 w/o plutonium on the alumina. The bed materials were screened to select the largest particles of the nominal 120-mesh alumina. The

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\*Pall Corp., Micro Metallic Division, Maywood, Illinois.

fraction retained on a 100-mesh screen (about 5% of the original bed) was used in these experiments. Photomicrographs of the alumina contained in this 100-mesh fraction showed that the particles were very irregular in shape.

The procedure used for the autoradiographic experiments was as follows: A small quantity of alumina, about 1 to 3 mg, was mounted in clear plastic\* and polished through 600-grit emery paper to expose a cross section of the alumina granules. Each mount containing the alumina particles was then cleaned in an ultrasonic bath to remove loose radioactive particles. This procedure was performed in a special alpha-handling metallurgical facility. The mounts were next moved to an open-faced hood and cleaned again, using first a soap solution and then a solution of Versene. Swipes taken of the surfaces of the mounts after this cleaning procedure showed no loose radioactive particles. The surfaces of the amounts were counted and showed 10,000 dis/min for the mount containing the 0.005 w/o plutonium-alumina, and 500,000 dis/min for the mount containing the 0.12 w/o plutonium-alumina. All other surfaces of the mounts showed less than 2000 dis/min. As a final precaution, the mounts were dipped in a 1.5% solution of vinyl plastic dissolved in methyl ethyl ketone to cover the surfaces with a thin layer of plastic. The mounted specimens were then moved to a darkroom, and Kodak AR-10 autoradiographic emulsions were placed in contact with the active surfaces of the mounts by the usual technique. Exposures of from 5 hr to 5 days were made, after which the radiographic emulsions were developed in place.



108-7234

Fig. 7. Micrograph of Autoradiographic Emulsion, Showing Alpha Tracks due to Plutonium on Surface of Fluid-bed Alumina

The emulsions were removed from the mounts and placed on microscope slides. Each autoradiograph of an individual alumina particle showed a dense band containing alpha tracks surrounding an area free of alpha tracks. Figure 7 is a micrograph of the emulsion, mounted on a microscope slide, after a 5-hr exposure of the alumina containing 0.12 w/o plutonium. The dark outlines are due to alpha particles and mark the shape of the

alumina grains; individual alpha tracks can be seen on the edges of the darkened areas. This micrograph clearly shows that the plutonium is present on the surfaces of the alumina particle.

\*Transoptic Mounting Powder (Lucite), Buehler, Ltd., Evanston, Illinois.



# G. Leaching of Plutonium from Alumina Used in Fluid Beds

A brief study was made to determine the efficiency of removal of plutonium from fluid-bed alumina by leaching with nitric acid. Recovery of plutonium by acid leaching is not expected to be a process operation, but was investigated only as a backup procedure if some malfunction should prevent removal of the plutonium by the fluorination method.

Alumina beds resulting from two different fluid-bed fluorination experiments were used in the leaching experiments. One of the alumina beds contained 0.011 w/o plutonium, 0.014 w/o uranium, 3.3 w/o iron, and 0.32 w/o chromium. The second alumina bed contained 0.118 w/o plutonium and 0.024 w/o uranium, but did not contain iron or chromium. The leaching solution used was 6N nitric acid-0.1 M aluminum nitrate. The aluminum nitrate is added to complex the fluoride ion and aid in the dissolution.

Leaching experiments were performed for 1, 3, and 5 hr at 100°C for each alumina bed. In each experiment, 50 g of the alumina bed were slurried with 100 ml of the nitric acid-aluminum nitrate solution. After the leaching period, the solution was decanted from the solid and filtered into a volumetric flask. The solution was then diluted to a known volume by adding additional quantities of the nitric acid-aluminum nitrate mixture used to rinse the solid residue at room temperature. The solution was sampled and submitted for plutonium and uranium analyses, and for iron and chromium analyses for samples in which these elements were present. The solid residue was dried, ground, and submitted for the same analyses. The filter papers were also submitted for plutonium analysis.

The data obtained from these two series of leaching tests are listed in Table XI. For the series of experiments using alumina bed 1, containing

TABLE XI. Recovery of Plutonium from Alumina Beds by Leaching with Nitric Acid

Leaching acid composition: 6N  $\text{HNO}_3$ -0.1M  $\text{Al}(\text{NO}_3)_3$

Composition of bed used: 50 g containing:

Bed 1: { 5.5 mg Pu (0.011 w/o),  
7.0 mg U (0.014 w/o),  
1650 mg Fe (3.3 w/o), and  
160 mg Cr (0.32 w/o).  
Bed 2: { 59 mg Pu (0.118 w/o) and  
12 mg U (0.024 w/o).

Leaching Conditions Time, hr      Temp, °C		Total Weight and Percentage of Original Quantity of Elements in Alumina Found in Leach Solution								Pu Remaining in Alumina after Leach		
		Pu		U		Fe		Cr				
		mg	%	mg	%	mg	%	mg	%	w/o	mg	Percentage of Original Pu
A. Experiments Using Alumina Bed 1												
1	100	3.3	60	4.1	59	1170	69	110	69	0.003	1.4	25
3	100	4.2	76	5.3	76	1360	83	134	84	0.002	0.8	15
5	100	4.7	86	-	-	1440	87	141	88	0.002	1.2	22
B. Experiments Using Alumina Bed 2												
1	100	48	81	15	125	-	-	-	-	0.012	5.9	10
3	100	51	86	14	116	-	-	-	-	0.007	3.3	6
5	100	51	86	15	125	-	-	-	-	0.008	3.9	7

iron and chromium as well as plutonium and uranium (Section A of Table XI), the leach solutions contained 60, 76, and 80% of the original plutonium present on the alumina for the 1-, 3-, and 5-hr tests at 100°C, respectively. The corresponding solid residues contained 25, 15, and 22% of the original plutonium content of the alumina, corresponding to a reduction in the plutonium content of the alumina by about a factor of five from 0.011 w/o to about 0.002 w/o. The solutions contained 59 and 76% of the uranium originally present on the alumina for the 1- and 3-hr tests, respectively. The uranium data obtained for the 5-hr test gave an anomalous result (greater than 200% recovery) and was discarded. The solutions also contained 69, 83, and 87% of the iron and 69, 84, and 88% of the chromium for the 1-, 3-, and 5-hr tests, respectively.

For the series of experiments using alumina bed 2 (Section B of Table XI) in which the alumina did not contain iron or chromium, the leach solutions contained 81, 86, and 86% of the plutonium originally present on the alumina for the 1-, 3-, and 5-hr tests, respectively. The corresponding solid residues contained 10, 6, and 7% of the original plutonium content of the alumina, corresponding to a reduction in the plutonium content of the alumina by an order of magnitude from the original value of 0.118 to 0.010 w/o or less. Essentially all of the uranium contained on the alumina was removed in all three tests.

The total of plutonium recovered in the solutions and the solid residues in all of the tests did not equal the amount considered to be in the solid alumina at the start of the tests. This discrepancy may be due to actual variation in the plutonium contents of the various 50-g samples, or loss to the surfaces of the glassware used in handling the resulting solutions. The filter papers did not contain appreciable amounts of plutonium as was shown by analysis, which indicated only microgram quantities to be present. If the leaching recoveries are normalized to the quantity of plutonium actually found in the solutions and on the solid residues, then the recovery in the solutions are 71, 84, and 80% for alumina bed 1, and 89, 94, and 93% for alumina bed 2 for the 1-, 3-, and 5-hr tests, respectively.

These data indicate that a leaching process using nitric acid-aluminum nitrate solution would efficiently remove plutonium retained on alumina under the rather mild reaction conditions of 100°C and 5 hr exposure or less. For alumina beds containing approximately 0.1 w/o plutonium, the plutonium content can be lowered to 0.01 w/o or less. For an alumina bed containing about 0.01 w/o plutonium, the plutonium content would be reduced to 0.002 w/o.

#### IV. SUMMARY

Initial experimental work was concerned with exploring the reaction conditions necessary to effectively convert the uranium and plutonium content of  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixtures to their respective hexafluorides. The results indicated that a temperature of  $550^\circ\text{C}$  for reaction times of greater than 10 hr would be necessary to achieve effective removal of plutonium from an alumina fluid bed. To achieve levels of plutonium on the alumina of less than 0.01 w/o, the feeding-fluorination period was carried out at  $450^\circ\text{C}$  by using a gas phase containing 20% fluorine in nitrogen and was followed by recycle-fluorination periods (using 100% fluorine) of 5 hr at  $450^\circ\text{C}$ , 5 hr at  $500^\circ\text{C}$ , and 10 hr at  $550^\circ\text{C}$ . These reaction conditions were those found most effective in previous work in which small batches of materials were reacted by means of a boat-reactor system.<sup>2</sup>

The effect of the presence of a mixture of nonradioactive F.P. oxides on the retention of plutonium on alumina was investigated. The F.P. mixture contained  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{ZrO}_2$ , and  $\text{MoO}_3$ . The presence of the F.P. mixture in the  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  resulted in a substantial increase in the retention of plutonium on the alumina. The results obtained in the fluid-bed experiments were identical to those previously obtained in the boat-reactor study.<sup>2</sup>

The effect of various reaction conditions on the retention of plutonium on alumina was investigated. The results of these investigations are listed in the following discussion:

1. The effect of the source of plutonium in the  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixtures (whether from the oxidation of a solid solution of  $\text{PuO}_2$  in  $\text{UO}_2$  or from  $\text{PuO}_2$  mixed with  $\text{U}_3\text{O}_8$ ) on the retention of plutonium on alumina was evaluated. The results of experiments using both sources of plutonium did not show any effect on plutonium retention.

2. The addition of bismuth to the solid reaction mixture did not result in an increased removal of plutonium from the alumina.

3. Experiments were performed to determine the effect of the quantity of plutonium and fission products fed to the alumina bed upon the retention of plutonium on the alumina. The results of these experiments showed that a 7.5-fold increase in the plutonium fed to the reactor in a single experiment would result in a 20- to 50-fold increase in the plutonium retention on the alumina. Increasing the F.P. level 7.5-fold resulted in an increase in plutonium retention on the alumina by a factor between three and four.

4. The effect of flow rate of the fluorinating gas phase on the plutonium retention on alumina was investigated. Plutonium retention on the alumina was minimized with gas flow rate in excess of 6 liters/min.

Under static-bed conditions, with flow rates of less than 1 liter/min, the plutonium retention on alumina was unsatisfactorily high.

5. Plutonium removal was unaffected by the type of alumina (either Type RR, fused; or Type T-61, sintered), or by the particle-size distribution of the alumina.

The possible reuse of an alumina bed for several additions and fluorinations of nuclear fuel would have potential savings in alumina use and in the quantity of waste to be disposed of. Several reuse experiments were performed involving an many as eight additions and fluorinations to one alumina bed. The reaction conditions used for each feeding-fluorination cycle were: feeding-fluorination period, 450°C and a  $\text{U}_3\text{O}_8\text{-PuO}_2$  mixture feed rate of about 2 g/min using 20% fluorine; and recycle-fluorination periods (using 100% fluorine) of 450°C for 5 hr, 500°C for 5 hr, and 550°C for 10 hr. These conditions had been shown to result in removal of 96-98% of the plutonium in a single addition-fluorination cycle.

The results obtained in these experiments showed that the plutonium concentration on the alumina would reach a value corresponding to less than 1% of the total plutonium fed to the reactor after five or fewer reuses of the alumina bed. The results also indicated that the presence of molybdenum in the F.P. mixture did not result in increased plutonium retention on the alumina. Deterioration of the alumina, which if it occurred would limit the reuse of the alumina, was not detected by surface-area or fluoride-content measurements.

The effect upon the plutonium retention on the alumina of the presence of stainless-steel decladding product formed by the HF-promoted oxidation reaction was determined. The results showed that the presence of the decladding product did not increase plutonium retention on the alumina. It was further shown that essentially all of the iron stayed in the fluid bed, but that 60-70% of the chromium was volatilized along with the  $\text{UF}_6$  and  $\text{PuF}_6$  product. Indications are that the volatile chromium compound may have been chromyl fluoride ( $\text{CrO}_2\text{F}_2$ ).

In an effort to ascertain the degree of plutonium holdup in the fluid-bed reactor system, a series of blank experiments was performed. The results indicated that a plutonium concentration on the alumina of 0.003 to 0.004 w/o might be considered as a base concentration for any one experiment. Plutonium may also be retained in the reactor in the cake deposited on the sintered-nickel bayonet filters of the disengaging chamber. Analysis of the filter cake removed from a set of the filters showed about 0.09 mg of plutonium and 132 mg of uranium per square inch of filter surface. This quantity of plutonium corresponds to about 3.5  $\mu\text{g}$  of plutonium retained per square inch of filter surface per gram of  $\text{PuF}_6$  passed through the filters.

Autoradiographs were made of sectioned alumina particles from alumina beds used in the fluorination of  $U_3O_8$ - $PuO_2$ -F.P. mixtures. Micrographs of the developed autoradiographic emulsions showed clearly that the plutonium present on the alumina particle was exclusively in the surface and not distributed in the body of the particle.

A brief study was made to determine the efficiency of removal of plutonium from fluid-bed alumina by leaching with nitric acid. Removal of plutonium in this manner would permit increasing the recovery of plutonium in those cases in which the alumina bed had retained an appreciable portion of the plutonium fed to the reactor. The results indicate that plutonium retained on alumina could be efficiently removed under rather mild reaction conditions: 100°C and 5 hr exposure or less. For alumina beds containing approximately 0.1 w/o plutonium, the plutonium content can be lowered to 0.01 w/o or less. For an alumina bed containing about 0.01 w/o, the plutonium content can be lowered to 0.002 w/o.

## APPENDIX A

Technique of Sampling Alumina Beds and Analytical Methods Used  
to Determine Uranium and Plutonium Content1. Technique of Sampling Alumina Bed

After a fluorination experiment, the alumina bed was sampled to obtain plutonium and uranium analyses so that the extent of the fluorination reaction could be ascertained. It was necessary to assure that the sample of the bed taken for analysis was representative of the total bed material. A satisfactory technique of sampling was developed for this purpose and is described in this part of this appendix.

The alumina bed (about 570 g) was removed from the reactor and was placed in a polyethylene bottle, which was then rotated for 1 hr around its long axis. This tumbling action of the alumina in the bottle insured a homogeneous mixing of the fines and alumina. Following the mixing period, the bed was dumped out on a plastic sheet and a sample of about 5 g taken by coning and quartering the solid. This sample was then finely ground by means of a power-operated mortar and pestle and submitted for analyses.\*

To determine the representative nature of the withdrawn sample, duplicate samples were taken, the entire procedure being repeated for a series of alumina fluid beds. Three samples were taken from each of seven different fluid beds. The analytical results showed a variation of  $\pm 1.53\%$  in the plutonium content for alumina beds having total plutonium contents of 50 to 360 mg, and variation of  $\pm 6.63\%$  in the uranium content for alumina beds having total uranium contents of 10 to 120 mg. These data show that the sampling technique was adequate for this work.

2. Analytical Methods for Uranium and Plutonium

The finely ground alumina sample presented for analysis is first converted to a water-soluble form by fusion in a 50 w/o  $\text{NaCO}_3$ -50 w/o  $\text{Na}_2\text{BO}_3$  flux. About 0.5 g of the alumina is mixed with 2.5 g of the flux and heated to

\*The power mortar used for grinding the alumina samples was located in the alpha box containing the fluorination equipment. Since the input feed material was handled in the same area of the alpha box, cross-contamination of the fluid-bed alumina was a possibility. After each sample was ground, a portion of clean alumina was then ground in the agate mortar and pestle as a cleanup step to remove any contamination left by the grinding of the experimental sample. To determine the effectiveness of this cleanup step, several tests were made to determine the residual plutonium and uranium present in the mortar. This was done by grinding a portion of alumina immediately following the grinding of the cleanup-step alumina and submitting a sample for analysis. The average concentrations of plutonium and uranium for two such steps were 0.00036 and 0.0005 w/o, respectively. Since the lowest-concentration experimental samples contained about 10 times these levels, the residual plutonium and uranium remaining in the agate mortar and pestle would not contribute a significant bias to the experimental sample.



1000°C for 3 to 8 hr in a platinum crucible. If the alumina used for the fluid bed was Type RR, then the 8-hr heating time was needed; however, if Type T-61 alumina was used, then the 3-hr heating period was sufficient. The cooled melt resulting from the fusion was then dissolved in 3N HNO<sub>3</sub>.

Analyses for plutonium and uranium were then made using one or more of the following analytical methods.

a. Radiochemical Analysis for Plutonium

The solution resulting from dissolution of the melt in 3N HNO<sub>3</sub> was treated with hexone to separate plutonium from americium. A small portion of the hexone phase was plated on a metal planchet, and the alpha emission due to the plutonium was counted. The size of the plated sample was chosen to obtain at least 10<sup>4</sup> alpha counts per minute (about 0.2 μg of plutonium) at 2 pi geometry in an alpha gas proportional counter. The total count obtained in this manner was converted to counts/min/g of solid sample, which could then be converted to mg of plutonium per g of solid by using the specific activity of the plutonium used, taking into account the counting geometry.

b. Fluorometric Determination of Uranium

Another portion of the solution resulting from the dissolution of the melt in 3N HNO<sub>3</sub> was extracted with hexone with the addition of KI to prevent coextraction of plutonium. The hexone phase, containing essentially no plutonium, was then analyzed for uranium content by means of the standard fluorometric technique.

c. X-ray Spectrochemical Analysis

An X-ray spectrochemical procedure has been developed which provides rapid and reliable analysis for plutonium and uranium (and a number of other elements) in fluid-bed alumina.<sup>11</sup> A finely ground sample of the alumina bed is intimately mixed with an equal weight of fine plastic molding powder and cold-pressed in a hydraulic press. The resultant smooth, nonfrangible pellet is encased in a Mylar bag before presentation to the X-ray spectrometer. Analysis consists of comparing the uranium or plutonium L $\alpha$  X-ray emission-line intensities with those from a set of similar, chemically analyzed or specially prepared, standards. Figure 8 represents a typical X-ray spectrochemical scan of an alumina-molding powder pellet showing the L $\alpha$  lines for uranium and plutonium and a K $\alpha$  line for yttrium. The detection limit for uranium and plutonium is 0.006% (at the present point of development).

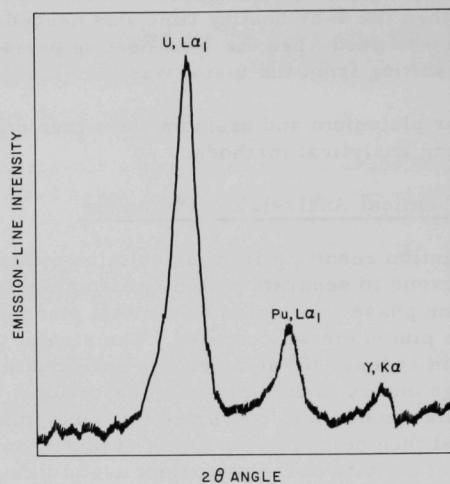


Fig. 8. Typical X-Ray Spectrochemical Scan

## APPENDIX B

Effect of  $\text{BiF}_3$  on the Fluorination Rates of  $\text{U}_3\text{O}_8$  and  $\text{UO}_2\text{F}_2$ 

A thermobalance study of the effect of the addition of  $\text{BiF}_3$  on the rates of fluorination of  $\text{U}_3\text{O}_8$  and  $\text{UO}_2\text{F}_2$  has been performed. The addition of small amounts of  $\text{BiF}_3$  to the  $\text{U}_3\text{O}_8$ - $\text{PuO}_2$  mixtures used in the fluid-bed experiments was considered as a means of obtaining better plutonium removal from the alumina during the fluorination (see Section III-B-3).

The Sartorius thermobalance was used for this work, which covered the range of 400-450°C and used a fluorine flow of 200 cc/min. The fluorination rates of  $\text{BiF}_3$ ,  $\text{U}_3\text{O}_8$ ,  $\text{UO}_2\text{F}_2$ , and the mixtures  $\text{BiF}_3$ - $\text{U}_3\text{O}_8$  and  $\text{BiF}_3$ - $\text{UO}_2\text{F}_2$  have been measured.

The  $\text{BiF}_3$  used in these experiments was shown by chemical analysis to contain 79.4% bismuth and 15.3% fluorine (calculated: 78.6% bismuth and 21.4% fluorine). The low result for the fluorine analysis indicates the presence of a bismuth oxide.

The results obtained in these experiments are listed in Table XII. The presence of 7.5 and 15%  $\text{BiF}_3$  in  $\text{U}_3\text{O}_8$  resulted in fluorination rates

TABLE XII. Fluorination Rates of  $\text{BiF}_3$ - $\text{U}_3\text{O}_8$  and  $\text{BiF}_3$ - $\text{UO}_2\text{F}_2$  Mixtures on a Thermobalance

Temperature: As indicated  $\pm 10^\circ\text{C}$   
Fluorine flow: 200 cc/min, 100%  $\text{F}_2$

Material	Temperature, °C	Fluorination Rate, mg/min
$\text{BiF}_3$	400	0.4
$\text{BiF}_3$	450	2
$\text{BiF}_3$	450	3
$\text{BiF}_3$	450	1.5
$\text{BiF}_3$	510	4
$\text{BiF}_3$	540	6
$\text{U}_3\text{O}_8$	390	0.8
$\text{U}_3\text{O}_8$	450	2
$\text{U}_3\text{O}_8$	450	2
$\text{U}_3\text{O}_8$	450	2
$\text{UO}_2\text{F}_2$	400	4
$\text{UO}_2\text{F}_2$	450	50
7.5 w/o $\text{BiF}_3$ -92.5 w/o $\text{U}_3\text{O}_8$	450	6-8
15 w/o $\text{BiF}_3$ -85 w/o $\text{U}_3\text{O}_8$	390	0.4
15 w/o $\text{BiF}_3$ -85 w/o $\text{U}_3\text{O}_8$	450	14
15 w/o $\text{BiF}_3$ -85 w/o $\text{U}_3\text{O}_8$	450	13
18 w/o $\text{BiF}_3$ -82 w/o $\text{U}_3\text{O}_8$	450	Too high to record
20 w/o $\text{BiF}_3$ -80 w/o $\text{U}_3\text{O}_8$	450	Too high to record
30 w/o $\text{BiF}_3$ -70 w/o $\text{U}_3\text{O}_8$	450	Too high to record
10 w/o $\text{BiF}_3$ -90 w/o $\text{UO}_2\text{F}_2$	400	3.5
20 w/o $\text{BiF}_3$ -80 w/o $\text{UO}_2\text{F}_2$	400	2.9
30 w/o $\text{BiF}_3$ -70 w/o $\text{UO}_2\text{F}_2$	400	2.3

at 450°C of 6 and 14 mg/min, respectively. Concentrations of  $\text{BiF}_3$  above 20% resulted in fluorination rates that were too rapid to follow on the recorder ( $>50$  mg/min). At 450°C,  $\text{BiF}_3$  and  $\text{U}_3\text{O}_8$  each have fluorination rates of about 2 mg/min. The addition of  $\text{BiF}_3$  to  $\text{UO}_2\text{F}_2$  resulted in fluorination rates at 400°C lower than those obtained for  $\text{UO}_2\text{F}_2$  itself. For  $\text{UO}_2\text{F}_2$ - $\text{BiF}_3$  mixtures, fluorination rates of 3.5 and 2.3 mg/min were obtained at 400°C for  $\text{BiF}_3$  contents of 10 and 30 w/o, respectively. The fluorination rates of  $\text{BiF}_3$  and  $\text{UO}_2\text{F}_2$  at 400°C are 0.4 and 4 mg/min, respectively.

In summary, the presence of  $\text{BiF}_3$  in  $\text{U}_3\text{O}_8$  greatly increases the rate of fluorination of  $\text{U}_3\text{O}_8$  in the range studied, 390 to 450°C. The fluorination rate of  $\text{U}_3\text{O}_8$  increases with an increase in  $\text{BiF}_3$  content. The presence of  $\text{BiF}_3$  in  $\text{UO}_2\text{F}_2$ , however, decreases the rate of fluorination of  $\text{UO}_2\text{F}_2$  at 400°C. The  $\text{UO}_2\text{F}_2$  fluorination rate decreases with an increase in  $\text{BiF}_3$  content.

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